Synthesis of Ethylamine
with a cw Tunable CO_2 Laser

Sun Mengjia, Yu Wengqian, Li Minqian, and Feng Xiaopeng

Research Group of Laser Chemistry, Institute of Optoelectronics, Shanxi University, Taiyuan, Shanxi, People's Republic of China

Abstract. The successful synthesis of ethylamine with a cw tunable CO_2 laser is reported. This action occurs at normal pressure ($\sim 5.32 \times 10^4$ Pa) and temperature ($< 100°$ C). No catalyst is used. The experiment shows a high directionality of this reaction. No other product except ethylamine is yielded. A possible mechanism for this reaction is discussed.

The process of traditional thermochemistry proceeds under the condition of thermodynamic equilibrium. The condition of reaction is usually critical; high temperature and high pressure are often necessary for the chemical reaction to occur. In most cases, a catalyst must be used. Owing to the isothermality of the process, a number of final products would be formed usually, thus the yield of product which is needed is relatively low. However, laser thermochemistry provides a new possibility. It tends to relieve the condition of reaction. It has usually the advantage of high directionality (or channel selectivity) in the process of reaction. For this reason, more attention has be paid to laser thermochemistry than before, not only to its physical mechanism, but also to its practical application in chemical synthesis. In this area, a few excellent reviews have already been written by Bunkin et al. [1, 2].

Some syntheses which have high directionality are based on ir multiphoton dissociation of molecules [3], for which a TEA-CO_2 laser is needed. For example, an organic synthesis of methylamine has been completed, which further demonstrated the potential of ir multiphoton chemistry [4]. Nevertheless, these processes belong to laser thermochemistry in their nature. The ir multiphoton absorption of a specific molecule at low gas pressure ($\leq 1.3 \times 10^3$ Pa) creates a free radical which has a high reactivity in chemical processes. Selective excitation of a specific bond of a reactant molecule ensures the channel selectivity to some extent

in the process of reaction, but a high intensity threshold must be reached.

However, this reaction can be completed by using a simple cw CO_2 laser with comparatively low average power [5]. Chen and Wang obtained monomethylamine with methanol and ammonia. No other product was yielded, thus channel selectivity was demonstrated in their experiment. They pointed out that the process of this reaction is a laser thermochemical one, but they have not explained the mechanism in detail yet. We think that the wavelength of a low-power CO_2 laser which is untunable may be randomly shifted, because the position of a single longitudinal mode within gain linewidth will move due to the thermal change of the short cavity. The radiation energy could not be efficiently absorbed by reactant molecules and the observation of monomethylamine is certainly related to the low conversion.

Is this a new type of reaction? What is the possible mechanism of this reaction? And why does this reaction have a better channel selectivity? Is this phenomenum a common one when we use the cw CO_2 laser to induce the reaction? In order to answer these questions we choose the synthesis of ethylamine to develop continuously the application of laser thermochemistry:

$$C_2H_5OH + NH_3 \rightarrow C_2H_5NH_2 + H_2O .$$
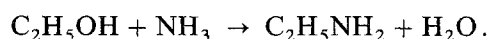
In general, the industrial synthesis of ethylamine proceeds at a high temperature (300-500° C) and high

pressure (~ 100 atm). A catalyst (Al_2O_3) must be used in this reaction. The products of this traditional chemical process are mixed one; they include ethyl-amine, diethylamine, and triethylamine. Because their physical properties are similar, it is difficult to separate them by conventional methods [6].

However, we initiated the system of $NH_3-C_2H_5OH$ with a cw frequency-tunable CO_2 laser with lower power under the condition of usual pressure ($\sim 5.32 \times 10^4$ Pa) and temperature ($< 100°$ C).

No catalyst was used. Analysis of the product has demonstrated that just monoethylamine is obtained. No diethylamine or triethylamine were yielded, demonstrating good channel selectivity again.

1. Experiment

The schematic drawing of our experimental device is shown in Fig. 1. The CO_2 laser is tuned at the wavelength of the P32 branch of the molecular spectrum (932.9 cm^{-1}), at which an ammonia molecule has a strong absorption (resonant absorption by lighter component). The laser has two beams – the zero-order line and first-order line. The powers at two window surfaces of the reaction which are made of KCl crystal are all about 6 W. The laser beams enter the reactor through two opposite ends so that the reaction can occur as homogeneously as possible along the axis. The spot size of the laser beams is about 5 mm, whereas the diameter of reactor is 10 mm and its length about 200 mm. In order to maintain the alcohol in the gaseous state, the reactor and the cell for vaporization are heated to 80 °C. The alcohol vapor and ammonia are premixed in the cell with the ratio of partial pressures 1:1. The gas mixture then flows into the reactor and keeps it at a pressure of $\sim 5.32 \times 10^4$ Pa. The reaction happens when the gas mixture is irradiated by laser light. The reaction product is
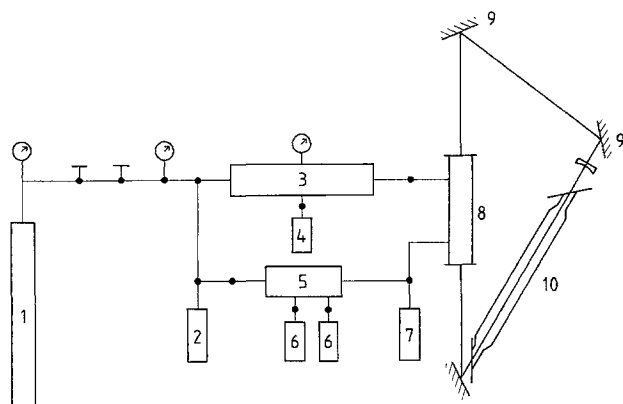
collected into a bottle with diluted hydrochloric acid, and then the sample is dried by distillation.

In order to examine whether the product contains only monoethylamine, three analytical methods are used: (a) The development reaction of tetrachloro-quinone with amine hydrochloride. The existence of amine in the sample can be detected. The ammonia does not disturb the analytical result in this reaction and the detection limit of amine is about 0.5 mg; (b) Hinsberg's reaction. This is a classical method of amine separation, and whether an amine is primary, secondary or tertiary is best established by the Hinsberg's test. When we treat an amine with benzenesulfonyl chloride and excess potassium hydroxide, we will observe the following phenomena: A primary amine yields a clear solution, from which, upon acidification, an insoluble compound, which is unaffected by acid forms. A tertiary amine yields an insoluble compound (the unreacted amine itself) which dissolves upon acidification of the mixture [7]. In our experiment Hinsberg's reaction shows that just monoethylamine (primary amine) is produced; (c) Infrared spectroscopy. We evaporate and dry the solution of hydrochloric acid which contains our product sample. Because the solubility of ammonium chloride and amine hydrochloride are different in waterless ethanol, the product mixture in our experiment can be gradually purified after many cycles, then the sample which contains more amine hydrochloride can be obtained. Using the conventional method of ir spectroscopy, the ir absorption spectrum of sample which contains amine hydrochloride and some ammonium chloride is obtained as shown in Fig. 2. Comparing this spectrum with the standard spectra of ethylamine hydrochloride or ammonium chloride, no characteristic absorption for diethylamine and triethylamine are found. Just as we expected, there is only monoethylamine produced in this reaction initiated by a cw tunable CO_2 laser. The results of these three analytical methods all agree.

2. Discussion

As mentioned above, the disadvantage of traditional synthesis of primary amine using alkylation of ammonia by alcohols is that alkylation can seldom be stopped sharply at the monoalkyl stage and mixtures with variable amounts of secondary, tertiary and even quaternary amines result. The simplest expedient to minimize this difficulty is to use a large excess of ammonia, so that the probability of the alkylating agent reacting with an ammonia molecule is much greater than the probability that it will react with a molecule of a previously formed amine. Nevertheless, it is still difficult to get a high purity product. However, both our synthesis of ethylamine and the synthesis of

Fig. 1. Schematic drawing of the experimental device (*1* NH$_3$, *2* vacuum pump, *3* cell, *4* alcohol, *5* collector, *6* absorption bottle, *7* N$_2$, *8* reactor, *9* mirror, *10* CO$_2$ laser
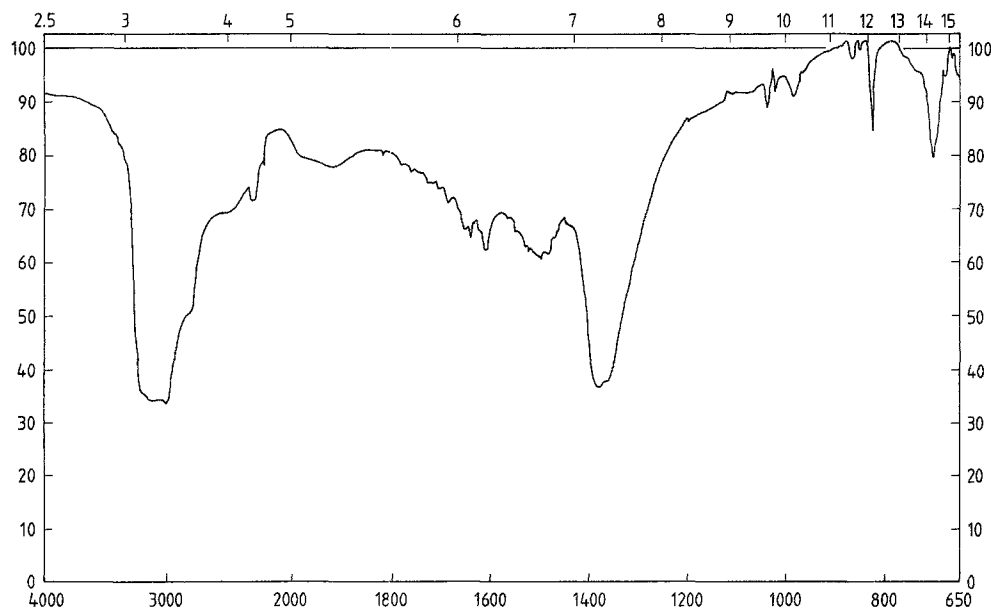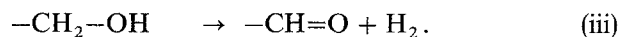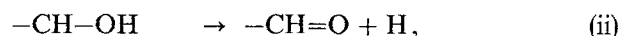
Fig. 2. Infrared spectrum of the sample produced in experiment

methylamine by Chen and Wang using a cw CO_2 laser demonstrated not only relieving of the reaction conditions, but also no need for a large excess of ammonia to obtain a pure monoamine.

From the chemical viewpoint, this would be a novel type of reaction. Because it is a homogeneous gas-phase reaction, it is self-evident that polar effects (ionic reaction) play no role. It doesn't need any catalyst except laser energy and it doesn't depend on the product as a catalyst; the reaction is not self-catalytic, so the catalytic reaction is not comparable. The only two reaction types to consider are radical reactions or concerted reactions. For a radical reaction, one must first ask for the weakest bond. This is the C—H bond in the $-CH_2-OH$ group. It is not the O bond and not the N—H bond, so a direct radical substitution is out of question. The C—H bond splitting is certainly followed by the thermal loss of the OH hydrogen which is compensated with the laser energy. This would be a radical chain reaction: (i) and (ii), although a concerted elimination (iii) can not be excluded,

$$-CH_2OH + H \rightarrow \dot{C}HOH + H_2, \qquad (i)$$

$$-CH-OH \quad \rightarrow -CH{=}O + H, \qquad (ii)$$

$$-CH_2-OH \quad \rightarrow -CH{=}O + H_2. \qquad (iii)$$

Aldehyde readily reacts with NH_3 at room temperature to form $-CH{=}NH$, which then can be reduced to the amine by the hydrogen atoms; the radicals formed can also take part in the chain reaction:

$$-\dot{C}H-NH_2 + -CH_2-OH \rightarrow$$

$$\rightarrow -CH_2-NH_2 + -\dot{C}H-OH. \qquad (iv)$$
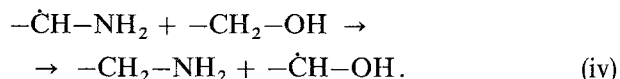
The total reaction has similarity to the "reductive amination" of aldehydes and especially to the variant, in which only a trace of aldehydes is used in the presence of the corresponding alcohol. The commercial alcohol always has a trace of aldehyde, possibly favoring this reaction. This reaction is usually performed in solvents favoring non-radical type, cyclic transition states. The novelty here is that reaction can also be stimulated by conditions favoring radical reactions.

From the view point of non-equilibrium physics, the mechanism of the reaction initiated by a cw CO_2 laser is different from that produced by non-equilibrium free radical due to ir multiphoton dissociation of molecules, although the synthetic result is like that produced in a ir photochemical process. Under irradiation of low power ir laser light, the energy of reactant molecules can only be raised to that of low lying vibrational excited states, not enough to break a bond of the molecule, because the energy of an ir photon which is absorbed by a reactant molecule is very low. At the normal pressure of gas mixture (such as $P \sim 5.32 \times 10^4$ Pa), the "vibrational temperature" is not far away from "translational temperature" due to the rapid V–T energy transfer from the molecular collision. The reaction system is heated, but it is not an equilibrium heating and the process is not isothermal. In particular, a feedback relationship between the temperature of the system and the concentration of ammonia molecules exists. In the case of resonant absorption by an ammonia molecule, the feedback has a particularly important role in the process. It is known from the theory of chemical phase transitions [8,9]

that the instability occurs when an intensity threshold is reached, and this results in a shift of the effective chemical equilibrium, favoring the forward reaction. Owing to the inhomogeneity of laser heating, various transportation processes in the system including diffusion, thermodiffusion and heat conduction, cannot be neglected. These will lead to the spatial inhomogeneity of the reaction. Along the axis of the reactor which is horizontal, the temperature is higher. The thermodiffusion features the lighter molecules moving to the incandescent zone, so the lighter molecules (NH_3) which absorb ir photons will move to axis resulting in a temperature gradient and concentration gradient further within the reactor volume. This spatial inhomogeneity decreases the intensity threshold for instability to occur, and this instability implies that certain chemical change happens. Because of this, a successful synthesis is obtained just by using a cw laser with comparatively low power.

In comparison, we synthesized monoethylamine in the case of non-resonant absorption. We tuned the laser at the wavelength of the 9R32 branch of the molecular spectrum ($1085.7\,cm^{-1}$) at which both ammonia and ethanol molecules have stronger absorption of laser energy, and the irradiation was kept the same as in the case of resonant absorption mentioned above. Analysis of the product sample shows that only monoethylamine was produced and the reaction still behaves as a single channel one, but the conversion is lower than that in the resonant case. On the one hand, this demonstrated that both cases (resonant or non-resonant) belong to the thermochemical regime; on the other hand, this indicates that the instability threshold in the non-resonant case is higher than in the resonant case (only the lighter component is the absorbed one) [1].

Laser heating is quite different from conventional heating. We heated the system up to $150°\,C$ for a long time without laser radiation, no amine was produced in the $C_2H_5OH-NH_3$ system. When the system was heated with laser radiation, the average temperature in the reaction volume was just about $150°\,C$ and amine is produced in the system. Chen and Wang imitated laser heating with an electrothermal wire heated to $200°\,C$; no monomethylamine was found, the reaction system was heated by laser beam, monoamine was produced. These facts indicate that the existence of the feedback decreases the activation energy of this reaction. However, it is a negative feedback between "chemical" and "thermal" degrees of freedom of the system. When the laser radiation above threshold acts on the system, the shift of chemical equilibrium leads to decrease in the concentration of reactant. This in turn, reduces the amount of laser energy absorbed by the reactant molecules, thus reducing the temperature of the system. Both reduction in temperature and in concentration lead to a decrease of the reaction rates. The increase of the product concentration will favor the reverse reaction. The system leaving the old equilibrium will arrive at a new equilibrium state and the reactant cannot be completely consumed. This is the reason why the yield of product is lower. In spite of this, the reaction process still has a good channel selectivity. This may be attributed to the following factors: (a) the activation energy for monoethylamine production is lower than that for diethylamine and triethylamine. (b) the concentration of monoethylamine in the reaction volume is not high; (c) the laser power in this experiment is comparatively low: it is not enough to initiate the reactions for producing diethylamine and triethylamine.

3. Conclusion

The synthesis of ethylamine with ammonia and ethanol is an important reaction of organic chemistry in the chemical industry. By this synthesis, we demonstrated once more that the laser thermochemical method is better than traditional methods of thermochemistry in the purity of product. This method relieves the conditions which reaction usually requires and allows one to efficiently control the pathway of the reaction by choosing the wavelength and output power of the laser. Therefore, it has the advantage of selectivity and directionality with the chemical reaction to some extent. We expect that a lot of syntheses could be done using laser thermochemistry, but much work has to be done in clarifying the reaction mechanism and in searching for practical methods of raising the yield of product.

References

1. F.V. Bunkin, N.A. Kirichenko, B.S. Luk'yanchuk: Izv. Akad. Nauk. SSSR. Ser. Fiz. **46**, 1150 (1982)
2. F.V. Bunkin, N.A. Kirichenko, B.S. Luk'yanchuk: Usp. Fiz. Nauk. **138**, 45 (1982)
3. V.N. Bagratashvili: Izv. Akad. Nauk. SSSR. Ser. Fiz. **47**, 1991 (1983)
4. Gong Mengxiong et al.: Appl. Laser **2**, No. 1 (1982)
5. Chen Minsheng, Wang Fengyun: Appl. Laser **5**, 101 (1985)
6. Melvin, J. Astle: *Industrial Organic Nitrogen Compounds*, Reinhold (New York 1961) p. 7
7. Robert Thornton Morrison and Robert Neilson Boyd: *Organic Chemistry* (2nd edn.) (Allyn and Bacon 1971) p. 760
8. F.V. Bunkin, N.A. Kirichenko: Dokl. Akad. Nauk. SSSR. **277**, 1357–1361 (1984)
9. Yu Wengqian, Li Minqian, Sun Mengjia: Chem. Phys. (to be published)