Photochemical Processes due to n-π and π-π* Transitions of 3-Picoline N-Oxide in the Vapor Phase*

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The photochemical reactions caused by an n-π^* or a π-π^* transition of pyridine *N*-oxide and 2-picoline *N*-oxide were previously studied in the vapor phase[1,2], by irradiating with the 3261 Å (Cd $^3P_1$) or 2537 Å (Hg $^3P_1$) resonance line, respectively. As reported in the previous paper[2], the introduction of the 2-methyl group in pyridine *N*-oxide strongly influences the photochemical behavior of pyridine *N*-oxide both in n-π^* and π-π^* transitions. However, it is considered that the photochemical reactions of 3-picoline *N*-oxide are similar to those of pyridine *N*-oxide, because the hyperconjugative effect and also the interaction with the N→O group could be neglected with the 3-methyl group. Therefore, the present author has attempted the gaseous photolysis of 3-picoline *N*-oxide by irradiation with 3261 Å (Cd $^3P_1$) and 2537 Å (Hg $^3P_1$) resonance lines, each of which corresponds respectively to the absorption region due to an n-π^* or a π-π^* transition of 3-picoline *N*-oxide.

Experimental

The synthesis of the 3-picoline *N*-oxide used in this experiments was done by a method similar to that of pyridine *N*-oxide*2. The product was purified by vacuum distillation several times[3]. B. p., 123°C/5 mmHg.

The light sources employed for the photolysis in the n-π or π-π^* absorption region were a pyrex cadmium resonance lamp or a quartz mercury resonance lamp, respectively, which were used in the case of pyridine *N*-oxide[1] and 2-picoline *N*-oxide[2].

Since the experimental methods are similar to those of pyridine *N*-oxide and 2-picoline *N*-oxide as reported in a previous paper[1], the description of the experimental techniques are omitted in this paper. The photolytic products were divided into fractions A, B, C and D just as in the photolysis of pyridine *N*-oxide or 2-picoline *N*-oxide, where

Fraction A: Gaseous products not condensed at −196°C (liquid nitrogen).

Fraction B: Gaseous products condensed at −196°C and not condensed at −95°C (liquid nitrogen in methanol)

Fraction C: Liquid products condensed at −95°C and not condensed at −75°C (dry ice in methanol).

Fraction D: Dark brown polymers.

The pressures of fractions A and B were each measured with a Toepler-gauge, and analyzed by using a mass-spectrometer and a low pressure gas-chromatograph (column: benzyl ether). The analysis of fraction C was done with a Shimadzu

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1) N. Hata and I. Tanaka, *J. Chem. Phys.*, in press.

2) N. Hata, This Bulletin, 34, 1440 (1961).

3) E. Ochiai, *J. Org. Chem.*, 18, 534 (1953).

*2 The 3-picoline used in the synthesis of 3-picoline *N*-oxide was supplied by Dr. T. Kubota, to whom the author's thanks are due.

quartz spectrophotometer QB-50 and also a Shimadzu gas-chromatograph (column: cetyl alcohol). The analysis of fraction D was not carried out.

Results and Discussion

3-Picoline *N*-oxide has two absorption systems in the region of the near ultraviolet both in the solution of a non-polar solvent and in the vapor[4]. Figure 1 shows the absorption curves of 3-picoline *N*-oxide in the vapor phase, which was measured with a Cary recording spectrophotometer 14 M*[3]. As seen from Fig. 1, there are two absorption regions between 28000 and 40000 cm^{-1}, one of which is the weak absorption at about 30000 cm^{-1} and the other a stronger absorption at about 35500 cm^{-1}. As will be described in a later paper[4], the weak absorption at the longest wavelength which consists of sharp vibrational structures having an O–O band at 29368 cm^{-1} corresponds to the n-π^* absorption due to an excitation of non-bonding electrons localized on the oxygen atom to the antibonding π-orbital. On the other hand, the strong absorption having its absorption maximum at about 35703 cm^{-1} is considered to be due to a π-π^* transition.

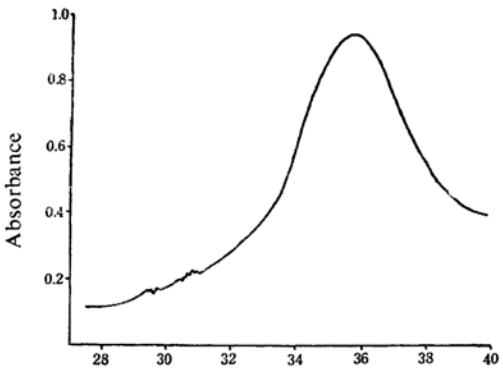


Fig. 1a. Vapor spectrum of 3-picoline *N*-oxide at 70°C. (Absorption region due to n-π^* and π-π^* transitions.)

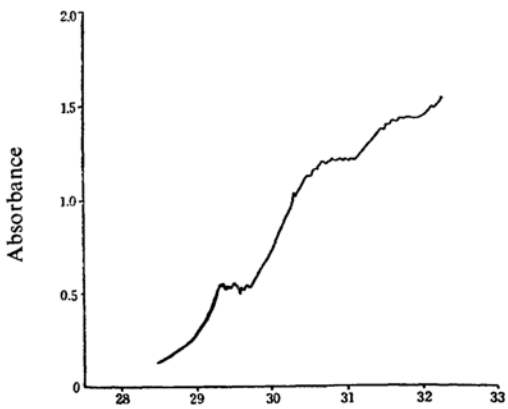


Fig. 1b. Vapor spectrum of 3-picoline *N*-oxide at 100°C. (Absorption region due to n-π^* transition.)

As described in the experimental part, the photolytic products due to irradiation with 3261 or 2537 Å were divided into fractions A, B, C and D. Fraction A was largely hydrogen, although small amounts of oxygen were detected in this fraction. Fraction B was identified as carbon dioxide. Fraction C, obtained as a liquid product, was 3-picoline. The experimental results were expressed as the quantum yield of fractions A, B and C at different temperatures as shown in Figs. 2 and 3. The quantum yields of the products at temperatures greater than 160°C were not shown in these figures, because the thermal decomposition of 3-picoline *N*-oxide occurs simultaneously with the photochemical decomposition at these higher temperatures.

The experimental results of the photolysis for 3-picoline *N*-oxide are summarized as follows.

a) A Relation between the Quantum Yield of Fraction C (3-Picoline) and the Temperature. —In the case of 3261 Å irradiation (n-π^* transition), the quantum yield increases markedly at about 80~100°C, although it has a comparatively low value at temperatures below 80°C. A further increase of the temperature causes a decrease in the quantum yield to some extent. On the other hand, the quantum yield at 2537 Å irradiation (π-π^* transition) is independent of the temperature, and has a value of about 0.55.

b) A Relation between the Quantum Yield of Fraction A (Mainly Hydrogen) or Fraction B (Carbon Dioxide) and the Temperature. — The quantum yields of fractions A and B increase continuously with rising temperature with both 3261 and 2537 Å irradiation.

c) In either case (i.e., 3261 and 2537 Å) comparatively greater amounts of fraction D (dark brown polymer) are obtained.

d) When the photolysis of a mixture of 3-picoline *N*-oxide and oxygen was carried out at different pressures of oxygen, the amount of fraction B markedly increased with increasing oxygen pressure, but that of fraction C decreased.

From the experimental results described above, it is concluded that the photochemical reaction of 3-picoline *N*-oxide is quite similar to that of pyridine *N*-oxide, but not to that

4) N. Hata, This Bulletin, to be published.

*3 The spectral measurement was performed by Dr. A. Kuboyama, to whom the author's thanks are due.

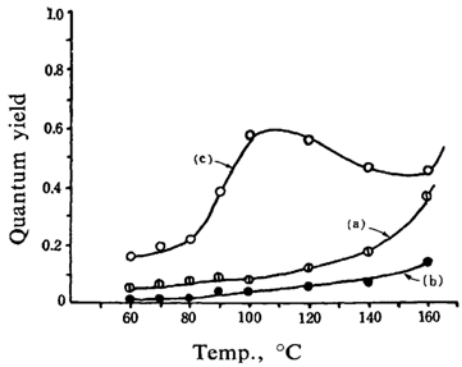


Fig. 2. Quantum yields of products versus temperature in the case of 3261 Å irradiation.
(a) —◐—: Fraction A
(b) —●—: Fraction B
(c) —○—: Fraction C

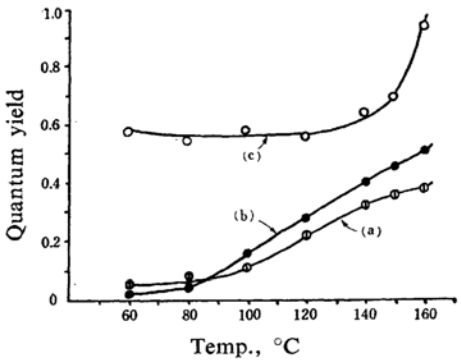
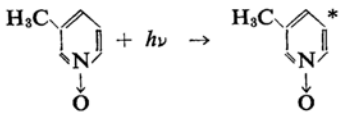
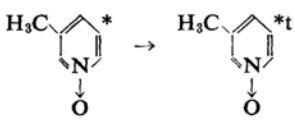


Fig. 3. Quantum yields of products versus temperature in the case of 2537 Å irradiation.
(a) —◐—: Fraction A
(b) —●—: Fraction B
(c) —○—: Fraction C

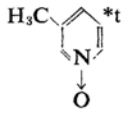
of 2-picoline *N*-oxide. This fact suggests that the hyperconjugative effect of methyl group or the interaction between N→O group and methyl group may be neglected in the photolysis of 3-picoline *N*-oxide. Therefore, it may be considered that the mechanism of the photochemical reaction of 3-picoline *N*-oxide would be similar to that of pyridine *N*-oxide. Thus, we assumed the following mechanism as the processes succeeding to an n-π^* and a π-π^* transitions of 3-picoline *N*-oxide.



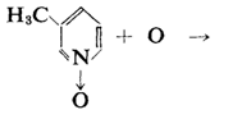
(1)



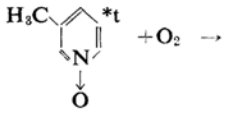
(2)



(3)



(4)



(5)

(* and *t denote the excited singlet and triplet states, respectively.)

First the 3-picoline *N*-oxide molecule is excited to the corresponding excited singlet state due to an n-π^* or a π-π^* transition caused by an absorption of 3261 or 2537 Å radiation. (Cf. the schematic potential curves for pyridine *N*-oxide as depicted in Fig. 4 of Ref. 1 for the succeeding description). Such an excited molecule probably decomposes to 3-picoline and atomic oxygen in a predissociative manner, in which a triplet state crossing with the first excited state exists presumably as a short lived intermediate. As seen from Figs. 2 and 3, the quantum yield of 3-picoline at 3261 Å irradiation shows a remarkable temperature dependence as pointed out in the experimental results a, while at 2537 Å irradiation it is independent of the temperature. This fact means that activation energy would be required for the production of 3-picoline at 3261 Å, but not at 2537 Å. The activation energy necessary for the production of 3-picoline in the case of 3261 Å irradiation is about 11.5 kcal. mol^{-1}, which was estimated from the relation between the quantum yield of produced 3-picoline and the temperature, and this value coincides nearly with that of pyridine *N*-oxide. Of the processes 3 and 4, which are possibly the essential reactions producing 3-picoline, the process 3 might be the only reaction requiring an activation energy. If an appreciable activation energy is required for process 4, the quantum yield of 3-picoline must also depend on the temperature even at 2537 Å irradiation. (However, the experimental results do not show any temperature-dependence of the quantum yield of 3-picoline at 2537 Å irradiation). As reported in a previous paper for the case of 2-picoline *N*-oxide[2], the temperature-dependence of the quantum yield of 2-picoline observed at 2537 Å irradiation was attributed to the interaction between the 2-methyl group and the N→O group as one of the main factors. Therefore, in the case of 3-picoline *N*-oxide the experimental result obtained at 2537 Å irradiation

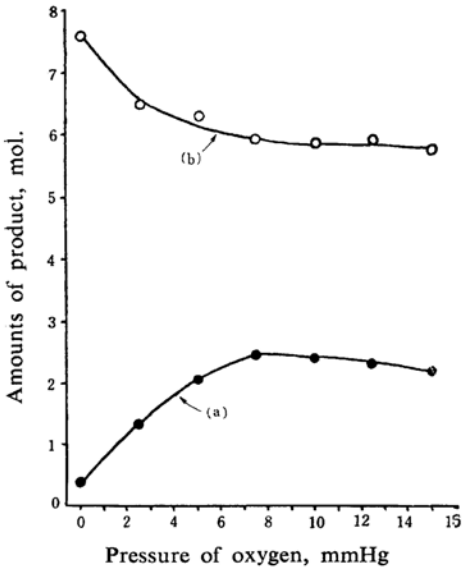


Fig. 4. Amounts of products versus oxygen pressure in the photolysis of mixtures of 3-picoline *N*-oxide and oxygen at 3261 Å (irradiation time: 2 hr., temperature: 100°C).
(a) —●—: Fraction B
(b) —○—: Fraction C

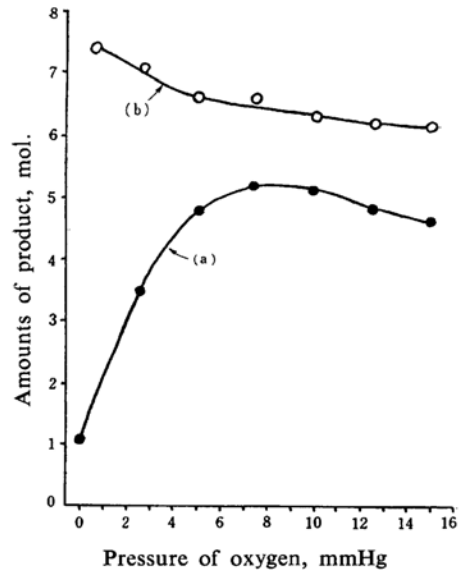


Fig. 5. Amounts of products versus temperature in the photolysis of mixtures of 3-picoline *N*-oxide and oxygen at 2537 Å (irradiation time: 10 min., temperature: 80°C).
(a) —●—: Fraction B
(b) —○—: Fraction C

(which is similar to that of pyridine *N*-oxide) supports the idea of the importance of the interaction between 2-methyl group and N→O group in the photolysis of 2-picoline *N*-oxide.

The results of the photolysis of mixtures of constant amounts of 3-picoline *N*-oxide and different pressures of oxygen are shown in Figs. 4 and 5 for the cases of 3261 and 2537 Å irradiations, respectively. These results indicate that the amounts of 3-picoline decrease and that of fraction B (carbon dioxide) increases with increasing oxygen pressure. This is regarded as evidence for the occurrence of the reaction 5 between the excited molecule and oxygen. In Figs. 4 and 5, the tendency for the amounts of products observed at oxygen pressures greater than about 7.5 mmHg to approach a saturated value may be ascribed to collisional deactivation of the excited molecule by oxygen with increasing pressures of oxygen.

Summary

Gaseous photolysis of 3-picoline *N*-oxide was attempted by irradiation with the 3261 Å (Cd $^3P_1$) or 2537 Å (Hg $^3P_1$) resonance line corresponding to an n-π^* or a π-π^* absorption region, respectively, of this substance. In either case, the photolytic products were mainly 3-picoline, and we observed a remarkable temperature-dependence for the quantum yield of 3-picoline in the case of 3261 Å irradiation but not in the case of 2537 Å irradiation. This observation suggests that an activation energy would be required for the production of 3-picoline at 3261 Å only. The activation energy estimated from the relation between the quantum yield of produced 3-picoline and the temperature at 3261 Å irradiation was about 11.5 kcal. mol^{-1}, which is almost about the same value as that of pyridine *N*-oxide. The reactions succeeding to an n-π^* or a π-π^* transition of 3-picoline *N*-oxide were considered to be similar to the case of pyridine *N*-oxide.

In conclusion, the author wishes to express his hearty thanks to Professor Ikuzo Tanaka for his kind guidance and encouragement. Thanks are also due to Mr. Y. Mori and to Dr. K. Naiki for their helpful discussion during the course of this work.

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