Photochemical Processes due to n-π^* and π-π^* Transitions of 2-Picoline N-Oxide in the Vapor Phase

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As reported in the previous paper1), the main photolytic product of pyridine *N*-oxide due to irradiation by 3261 or 2537 Å was pyridine in both cases. We observed a remarkable difference in the relation between the quantum yield of pyridine produced and the temperature.

In the case of 2-picoline *N*-oxide, however, it may be expected that the introduction of a methyl group in the 2-position of the pyridine ring might cause photochemical behavior different from that of pyridine *N*-oxide. In order to investigate the effect of 2-methyl substitution on the photolysis of pyridine *N*-oxide, the present author carried out the gaseous photolysis of 2-picoline *N*-oxide by irradiating with the 3261 Å (Cd $^3P_1$) or 2537 Å (Hg $^3P_1$) resonance line, which corresponds to absorption due to an n-π^* or a π-π^* transition of this substance, respectively. It was found from this experiment that 2-picoline *N*-oxide undergoes a photochemical rearrangement to isomerize to 2-pyridinemethanol at 3261 Å and a fission of N→O bond to produce 2-picoline at 2537 Å.

Experimental

The 2-picoline *N*-oxide used in this experiment was prepared by the method described by Ochiai and purified by vacuum distillation several times2). B. p., 105~106°C/4 mmHg.

A pyrex cadmium resonance lamp was used as a light source for the photolysis in the n-π^* absorption region, while a quartz mercury resonance lamp was used in the π-π^* absorption region, and these lamps were those used for the photolysis of pyridine *N*-oxide.

The gaseous photolysis of 2-picoline *N*-oxide was carried out by a procedure similar to that of pyridine *N*-oxide described in the previous paper1). Photolytic products were also divided into fractions A, B, C and D just as those of pyridine *N*-oxide, where

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

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

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

Fraction D: Dark brown polymer.

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 quartz spectrophotometer QB-50 and also a Shimadzu gas-chromatograph GC-1A (column: cetyl alcohol). The analysis of fraction D was not carried out.

Results and Discussion

The ultraviolet absorption spectra of several methylpyridine *N*-oxides have been measured in polar solvents by Ikekawa et al.3), where they discussed a relation between the maximum of π-π^* absorption and the position of the methyl group in the pyridine ring. The author has also observed a weak shoulder absorption

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

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

3) N. Ikekawa and Y. Sato, *Pharm. Bull.*, **2**, 400 (1954).

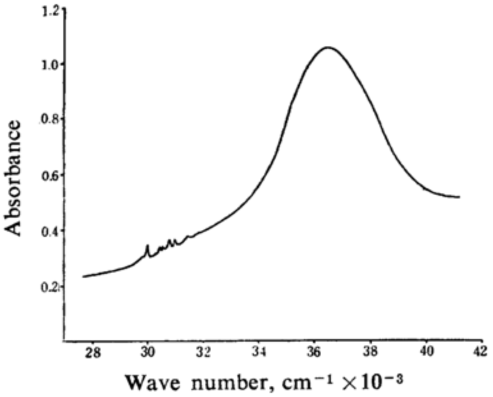


Fig. 1a. Vapor spectrum of 2-picoline *N*-oxide at room temperature. (Absorption region due to n-π^* and π-π^* transition.)

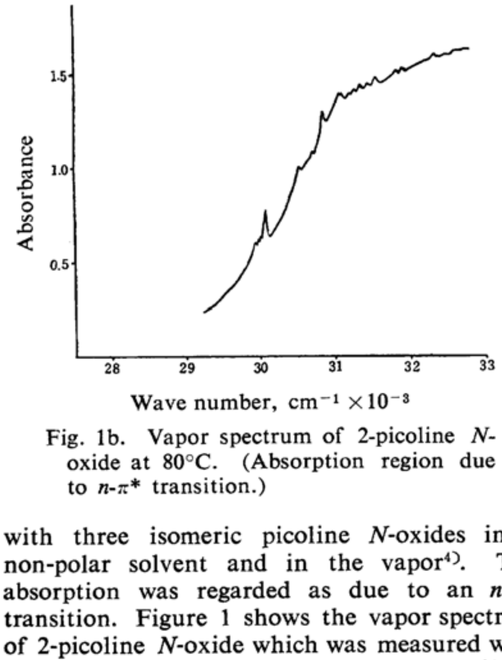


Fig. 1b. Vapor spectrum of 2-picoline *N*-oxide at 80°C. (Absorption region due to n-π^* transition.)

with three isomeric picoline *N*-oxides in a non-polar solvent and in the vapor[4]. The absorption was regarded as due to an n-π^* transition. Figure 1 shows the vapor spectrum of 2-picoline *N*-oxide which was measured with a Cary recording spectrophotometer 14 M[*2].

As described in the experimental part, the photolytic products at 3261 or 2537 Å irradiation were divided into fractions A, B, C and D. Fraction A was mainly hydrogen but included a small amount of oxygen, and fraction B was identified as carbon dioxide. Fraction C obtained as a liquid product was 2-pyridinemethanol at 3261 Å irradiation, whereas it was 2-picoline in the case of 2537 Å irradiation. The experimental results were expressed as quantum yields of fractions A, B and C at different temperatures as shown in Figs. 2 and 3.

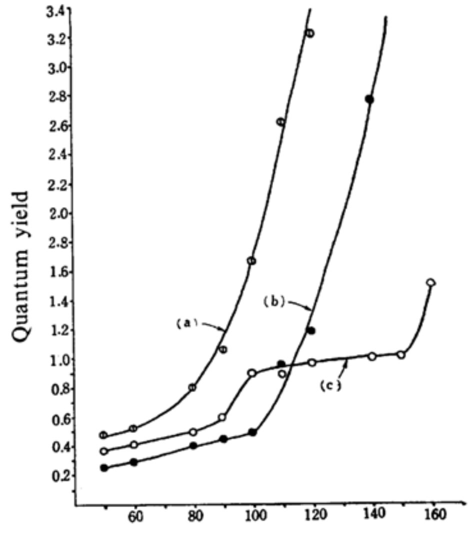


Fig. 2. Quantum yields of products versus temperature in the case of 2537 Å irradiation.
(a) —⦶—: Fraction A
(b) —●—: Fraction B
(c) —○—: Fraction C

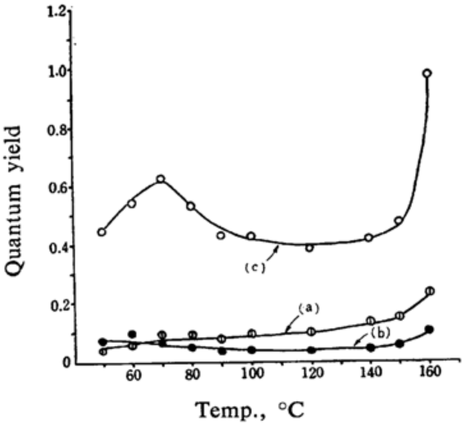
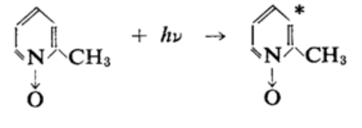


Fig. 3. Quantum yields of products versus temperature in the case of 3261 Å irradiation.
(a) —⦶—: Fraction A
(b) —●—: Fraction B
(c) —○—: Fraction C

The processes succeeding to a π-π^* transition of 2-picoline *N*-oxide may be expressed as follows, assuming that the excited molecule passes through a triplet state as in the case of pyridine *N*-oxide[1]. That is,



(1)

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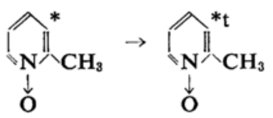
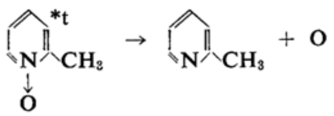
[4] N. Hata, This Bulletin, to be published.

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



(2)



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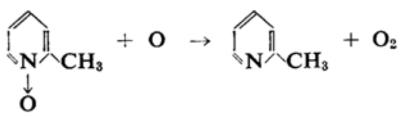

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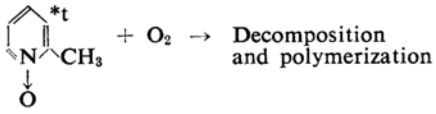
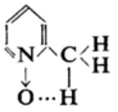


(5)

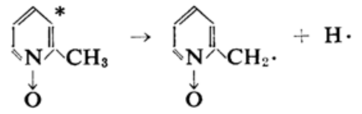
(* and *t denote the excited singlet and triplet states, respectively.)

Fig. 2 indicates how the quantum yield of each photolytic product at 2537 Å irradiation changes with temperature. Although the quantum yield of fraction C (2-picoline) is 0.4~0.5 at low temperatures, it increases steeply at about 90°C to a saturated value (0.9~1.0) at temperatures above 100°C. (Such a temperature dependence of the quantum yield has not been observed in the case of pyridine *N*-oxide at 2537 Å irradiation, in which case the quantum yield of pyridine produced did not change substantially with temperature.) This observation suggests that an activation energy would be required for the production of 2-picoline. This may be interpreted qualitatively as follows. Excited 2-picoline *N*-oxide, due to a π-π^* transition, presumably passes into a triplet state crossing with the excited singlet state to dissociate to 2-picoline and atomic oxygen in a predissociative manner as in the case of pyridine *N*-oxide (cf. Fig. 3 in Ref. 1). Since, for the pyridine *N*-oxide⁽¹⁾ or 3-picoline *N*-oxide⁽⁵⁾ which does not possess a methyl group in the 2-position of the pyridine ring, the quantum yield of fraction C is independent on the temperature, the temperature dependence observed in the case of 2-picoline *N*-oxide must be associated with the interaction between the methyl group and the N→O group. The N→O bond energy of 2-picoline *N*-oxide is approximately the same as in pyridine *N*-oxide, i. e. ca. 110 kcal. mol^{-1}, although it may be smaller than 110 kcal. mol^{-1} owing to the decrease of N→O double bond character caused by the hyperconjugative effect of 2-methyl group. Therefore, the process 3, by which the excited triplet 2-picoline *N*-oxide dissociates to 2-picoline and atomic oxygen, possibly does not need an activation energy. Thus, process 4 which is the alternative reaction producing 2-picoline is probably influenced by the interaction between the 2-methyl group and the N→O group. Investigation of the ultraviolet absorption spectrum of 2-picoline *N*-oxide⁽³,⁴⁾, suggests the formation of a weak hydrogen bond between the methyl group and N→O group as shown in A. Such a weak hydrogen bond formation may bring about a retarding effect for process 4 at low temperatures. Since the hydrogen bond is broken by the thermal perturbation caused by the increasing temperature, however, the abstraction reaction 4 would be facilitated by increasing temperature. Therefore, it is expected that the quantum yield of 2-picoline may rapidly increase to become about twice the value at low temperature. Figure 2 indicates distinctly the existence of such a tendency. The activation energy necessary for the production of 2-picoline estimated from the temperature-dependence of the quantum yield is about 1.1 kcal. mol^{-1}.



(A)

2-Picoline *N*-oxide gives rise also to substantial amounts of hydrogen upon irradiation with 2537 Å, where the quantum yield increases remarkably with rising temperature as shown in Fig. 2. This is probably due to a participation of the following processes in addition to the process 5.



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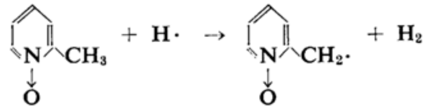

(7)

Although D(CH_2-H) in 2-picoline *N*-oxide is not known, it is reasonable to assume processes 6 and 7, since the gaseous photolysis of toluene produces hydrogen⁽⁶⁾.

In addition to processes 6 and 7, the production of fractions A, B and D probably resulted from the process 5 between excited 2-picoline *N*-oxide and oxygen produced by process 4 as in the case of pyridine *N*-oxide. To confirm the correctness of this reaction the gaseous photolysis was attempted for the mixture of 2-picoline *N*-oxide and oxygen, expecting that the 2-picoline would decrease and other products

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5) N. Hata, This Bulletin, **34**, 1444 (1961).

6) R. R. Hentz and M. Burton, *J. Am. Chem. Soc.*, **73**, 536 (1953); G. Porter, *Chem. Soc.* (*London*), *Spec. Publ.* p. 139, No. 9 (1957).

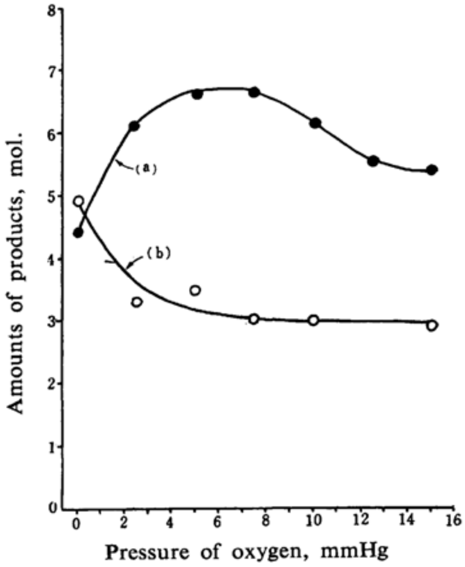


Fig. 4. Amounts of products versus oxygen pressure in the photolysis for the mixture of 2-picoline *N*-oxide and oxygen at 2537 Å (irradiation time: 10 min., temperature: 90°C).
(a) —●—: Fraction B
(b) —○—: Fraction C

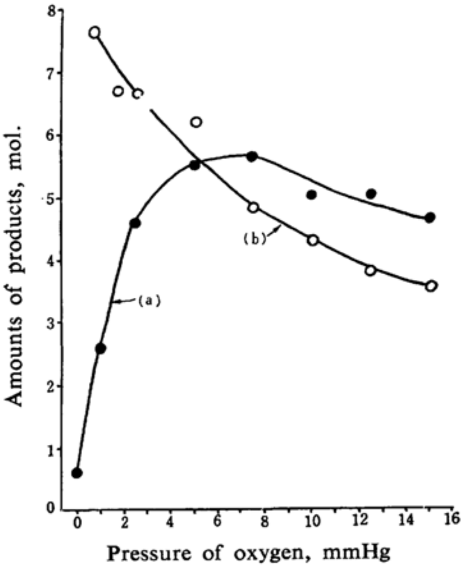
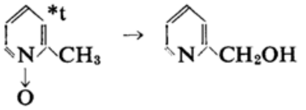


Fig. 5. Amounts of products versus oxygen pressure in the photolysis for the mixture of 2-picoline *N*-oxide and oxygen at 3261 Å (irradiation time: 2 hr., temperature: 70°C).
(a) —●—: Fraction B
(b) —○—: Fraction C

would increase with increasing oxygen pressure. The experimental results are expressed as amounts of fractions B (carbon dioxide) and C (2-picoline) in the decomposed products under the different pressures of oxygen. The results support clearly the occurence of process 5 described above.

In the case of 3261 Å irradiation (n-π^* transition), 2-picoline *N*-oxide isomerizes to 2-pyridinemethanol by a rearrangement of the oxygen atom of N→O group to the methyl group as shown in process 8 and the production of fractions A, B and D were very small.



(8)

As seen from Fig. 3, the quantum yield of fraction C shows a maximum value at about 70°C and approximate temperature-independence at temperatures greater than 100°C. The fact that the quantum yield is affected by changes in temperature seems to indicate that process 8 requires some activation energy. Its activation energy estimated from the quantum yield and the temperatures[*3] is about 3.4 kcal. mol^{-1}. This production of 2-picoline from its *N*-oxide at 3261 Å irradiation requires, presumably, an activation energy of about 11～12 kcal. mol^{-1}, considering the fact that the activation energy for the production of pyridine(1) or 3-picoline(5) from its *N*-oxide is about 11～12 kcal. mol^{-1}. Since the activation energy necessary for the photoisomerization of 2-picoline *N*-oxide to 2-pyridinemethanol is estimated to be about 3.4 kcal. mol^{-1}, however, the excited triplet molecule resulting from 3261 Å irradiation may largely undergo process 8 involving a smaller potential barrier than that for the N→O bond split.

If the photochemical behavior due to n-π^* transition is only the rearrangement process described above, its products should be 2-pyridinemethanol alone. However, the fact that small amounts of decomposed and polymerized products are detected in the products as seen in Fig. 3 seems to indicate that processes 3—7 occur simultaneously with process 8. The experimental results of the photolysis for the mixture of constant amounts of 2-picoline *N*-oxide and different pressures of oxygen suggest that the above assumption is reasonable. That is, as seen from Figs. 4 and 5 the fact that fraction B increases rapidly and fraction C decreases with increasing pressures of oxygen

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[*3] The quantum yield of 2-pyridinemethanol (fraction C) decreases at temperatures above 80°C, which may probably be ascribed to the increase of quenching of the excited molecule with increasing pressures of 2-picoline *N*-oxide. Therefore, the calculation of the activation energy necessary for the production of 2-pyridinemethanol was performed by using some of the quantum yields at temperatures below 80°C.

may be regarded as evidence for the reaction between excited 2-picoline *N*-oxide and oxygen.

Summary

The gaseous photolysis of 2-picoline *N*-oxide was carried out by irradiation with the 3261 Å (Cd $^3P_1$) or 2537 Å (Hg $^3P_1$) resonance lines corresponding to an n-π^* or a π-π^* absorption of this substance, respectively.

In the case of 3261 Å irradiation, the major product was 2-pyridinemethanol, whose quantum yield showed a marked temperature-dependence. The activation energy necessary for the production of 2-pyridinemethanol was estimated to be about 3.4 kcal. mol^{-1}.

On the other hand, the photolytic products at 2537 Å irradiation were 2-picoline and other decomposition products and polymers. The quantum yield of 2-picoline showed a marked temperature-dependence, which may be attributed to the interaction between the 2-methyl group and the N→O group. The activation energy necessary for the production of 2-picoline was estimated to be about 1.1 kcal. mol^{-1}.

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 Dr. K. Naiki for their helpful discussions during the course of this work.

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