culation of $\Delta S_{nm}^{\ddagger}$. The positive value of $\Delta S_{nm}^{\ddagger}$ indicates that some amount of libration of water molecules occurs in the activation process of the hydrated ion. Since the melting entropy of ice is 5.26 eu (=1.46 kcal/273), about 0.8 ($\simeq$4.32/5.26) parts of water molecules are liberated from the hydrated ion.

References

(1) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," p. 477–551, McGraw-Hill, New York, 1941.

(2) H. Eyring and J. O. Hirschfelder, *J. Phys. Chem.*, **41**, 249 (1937).

(3) J. O. Hirschfelder, *J. Chem. Ed.*, **16**, 540 (1940).

(4) J. F. Kincaid, H. Eyring and A. E. Stearn, *Chem. Rev.*, **28**, 301 (1941).

(5) H. Eyring and F. Daniels, *J. Amer. Chem. Soc.*, **52**, 1472 (1930).

(6) H. R. Pruppacher, *J. Chem. Phys.*, **45**, 2061 (1966).

(7) M. Y. Mah, Master Thesis, Department of Materials Science and Engineering, University of Utah, 1972.

(8) J. R. Van Wazer, J. W. Lyons, K. Y. Kim and R. E. Colwell, "Visaosity and Flow Measurement, a Laboatory Handobck of Rheology," 2nd Ed., p. 192, John Wiley & Sons, Inc., New York, London, Sydney, 1966.

(9) J. D. Ferry, *Chem. Rev.*, **18**, 373 (1936).

(10) (a) B. Rabinowitch, *Z. Physik. Chem. (Leibzig)*, **145A**, 1 (1929); (b) M. Mooney, *J. Rheol.*, **2**, 210 (1931).

(11) S. Oka, "Rheology: Theory and Applications," p. 22–23, Academic Press, New York, 1960.

(12) See T. Erdey–Gruz, "Transport Rhenomena in Aqueous Solutions," p. 149, Jjohn Wiley & Sons, New York, 1974.

(13) W. Sutherland, *Phil. May*, **9**, 781 (1905).

(14) A. Einstein, *Ann. Physik*, **19**, 371 (1906).

(15) F. S. Ree, T. Ree and H. Eyring, *Ind. Eng. Chem.*, **50**, 1036 (1958).

(16) G. S. Hartley, *Phil. Mag.*, **12**, 473 (1931).

(17) A. Mauro, *Science*, **126**, 252 (1957).

(18) L. B. Tricknor, *J. Phys. Chem.*, **62**, 1483 (1958).

(19) B. J. Zwolinski, H. Eyring and C. E. Reese, *J. Phys. Colloid Chem.*, **53**, 1426 (1949).

(20) K. H. Laidler and U. E. Shuler, *J. Chem. Phys.*, **17**, 851, 856 (1949).

(21) M. Nagasawa and Y. Kobatake, *J. Phys. Chem.*, **56**, 1017 (1952).

(22) Reference 1, p. 184.

(23) K. H. Lee, J. G. Jee, M. S. Jhon and T. Ree, *J. Bioengineering*, **2**, 269 (1978).

(24) J. G. Jee, M. S. Jhon and T. Ree, *J. Korean Chem. Soc.*, **22**, 304 (1978).

(25) J. Padova, *J. Chem. Phys.*, **40**, 691 (1964).

(26) "Lange's Handbook of Chemistry," 12th Ed. (ed. J. A. Dean), p. 3–120 to 3.125, McGraw-Hill, New York, 1979.

Photochemical and Thermal Solvolysis of Picolyl Chlorides

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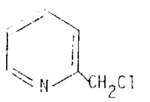
Photochemical and thermal solvolysis of 2,3,4–picolyl chlorides (2,3,4–PC) were studied in amine solvents and the results were correlated with the electronic structures calculated by PPP-SCF-MO CI method. Activation parameters show that the thermal solvolysis of PC is S_N2 type reaction. The rates of thermal reaction in pyridine or *t*–butylamine solvent decrease in the order of 2–PC>3–PC>4–PC. These results are consistent with the predictions based on the electron densities of picolyl chlorides. In photosolvolysis, the same products as those of thermal reactions were obtained. The results indicate that photochemical solvolysis undergoes through heterolytic cleavage. Relative quantum yields of photosolvolysis of 2,3,4–picolyl chlorides in *t*–butylamine solvent were determined to be 0.73, 1, and 0.50 respectively. These results are in good agreement with the electron densities of the excited triplet state of picolyl chlorides.

Introduction

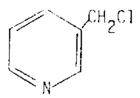
Interest in the photosolvolysis has been stimulated since the discovery that nitrophenyl phosphates and sulphates show a substitution reaction to yield the corresponding nitrophenol upon ultraviolet irradiation of their aqueous solutions[1]. There has been especially a considerable amount of work on the photosolvolysis of benzyl compounds in nucleophilic solvents since the photosolvolysis study of certain benzyl derivatives by Zimmerman and Sandel[2]. The compounds studied include benzyl (or substituted benzyl) sulfonium salts, ammonium salts, and halides. It has been reported that products resulting from both heterolysis and homolysis of the benzyl–heteroatom bond are formed either upon direct irradiation or upon photosensitization. When benzyl or substituted benzyl chlorides are photolyzed in *tert*-butyl alcohol, the sensitized reactions favored bond heterolysis and direct irradiations favored homolysis, although reactions are not clean in either case[3].

In contrary to benzyl halides, their heterocyclic analogues received virtually no attention. The nonbonding electrons of heteroatoms in the ring are expected to render some interesting effects on the solvolysis. Thus, the solvolysis and photosolvolysis of picolyl chlorides are studied in this investigation.

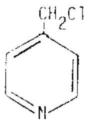
The nonbonding electron pairs on the nitrogen atom in picolyl chlorides are expected to render different electronic effects on the thermal and photochemical solvolysis of picolyl chlorides and this effect will be also different depending on the position of chloromethyl group on the pyridine ring of the compound.



2-picolyl chloride



3-picolyl chloride



4-picolyl chloride

The electronic structures of these three compounds will be determined by the MO calculations and thus obtained data, especially the charge distribution in both the ground and the first excited states, will be correlated to the experimental data of solvolysis and photosolvolysis.

The mechanism of the solvolysis in the ground state and excited states are expected to be different because of different electronic structures in two states and the S_N1 and S_N2 characters will also be different for two states of these three compounds as well as differing from each other among these compounds.

Experimental

Materials. Picolyl chloride hydrochloride (Aldrich Chemicals); 2-PC·HCl was recrystallized from ethanol-ether (mp. 125 °C), 3-PC·HCl was sublimed (mp 148 °C), and 4-PC·HCl was recrystallized from ethanol (mp 169 °C). Purified PC·HCl was dissolved in distilled water and neutralized with 10 % sodium bicarbonate solution. Free picolyl chlorides were extracted three times each with chloroform and dried with sodium sulfate. Evaporation of the solvent under the reduced pressure immediately prior to use yielded pure picolyl chlorides. *t*-Butylamine (Aldrich Chemicals) were dried over potassium hydroxide and distilled immediately prior to use taking only the middle portion (bp 45 °C). *sec*-Butylamine (Aldrich Chemicals) was purified by the same method used for *t*-butylamine. Pyridine (1st Grade, Wako Chemicals) were dried over potassium hydroxide and refluxed over barium oxide followed by distillation collecting only middle portion (bp 114.5 °C). All the other common solvents were purified by the known standard methods[4]. Piperylene (Aldrich Chemicals) was used as received.

Spectra. ^{1}H-Nuclear magnetic resonance spectra were measured on a Varian T-60A spectrometer against tetramethylsilane internal standard in D_2O, chloroform-d, or carbon tetrachloride. UV-VIS spectra were recorded on a Cary 17 spectrophotometer.

Nucleophilic Solvolysis of Picolyl Chlorides. Picolyl chloride (50 mg) and pyridine (5 m*l*) were reacted for 2h in a 40–50 °C bath. Chloroform and distilled water were added to the mixture and aqueous layer was separated, decolorized with activated charcoal and water was evaporated off to dryness to get colorless crystals. The solvolysis product was characterized by physical and chemical methods.

To determine the solvolysis rate constants, picolyl chloride (240 mg) was dissolved in pyridine (3 m*l*) and kept the solution in the constant temperature bath. The change of intensity of methylene proton peak of picolyl chlorides in the nmr spectrum was monitored against the constant pyridine proton peak varying the reaction time. When the logarithm of picolyl chloride concentration was plotted against time, a straight line was obtained and a first order rate constant was obtained from the slope.

Photochemical Nucleophilic Solvolysis. Picolyl chloride (40 mg) was dissolved in t-butylamine (3 m*l*) and irradiated in a quartz tube with 253.7 nm UV light in a Rayonet RPR 208 Photochemical Reactor (The Southern New England Ultraviolet Company) for 2h at 30 °C. Aqueous 10 % sodium carbonate solution was added to the sample and *t*-butylamine was distilled off and solvolysis product was extracted with chloroform, dried with anhydrous potassium carbonate, decolorized with activated charcoal. The product was analyzed quantitatively by ^{1}H nmr after the solvent was evaporated off under the reduced pressure.

Quantum Yield Measurements. Picolyl chlolides (80 mg) dissolved in *t*-butylamine (60 m*l*) and two portions of 3 m*l* of the solution were put into a quartz tube and a Pyrex tube. The Pyrex tube was wrapped with aluminum foil to cut off the light. Each tube was irradiated with 253.7 nm light for 30 minutes in a merry-go-round of Rayonet photochemical reactor RPR 208. After irradiation, the solvent was evaporated off and the residue was dissolved in carbon tetrachloride and analyzed by nmr spectrometry. Thus measured quantum yields were calibrated for the thermal solvolysis. The light intensity was monitored by ferrioxalate actinometry[5].

Quenching and Sensitization Studies. The same procedures were followed for quenching and sensitization studies as the procedures used for quantum yield measurements except adding quenchers and sensitizers respectively. Piperylene was used as a quencher and acetone was a triplet sensitizer with 300 nm excitation.

Molecular Orbital Calculation. Transition energies, electron densities, and bond orders were calculated by SCF MO-CI PPP (Pariser-Parr-Pople) method[6,7]. Six excited configurations were considered in the calculations for excited states.

The semi-empirical integrals used in computation are listed in Table 1.

The one-center repulsion integral, $\langle rr|rr\rangle$, was evaluated according to the Pariser-Parr approximation and the two-center integral, $\langle rr|ss\rangle$, was estimated by the Mataga-Nishimoto formula.[8]

TABLE 1: Semiempirical Integrals (inv eV)

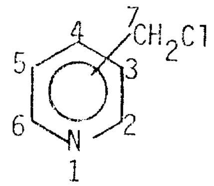
Atom	Bond, *rs*	Ionization potential ($-W_{2p}$)	(*rr*/*rrss*)
C	C=C	11.16	11.13
	C–C	9.0	10.87
N	C=N	14.12	12.34

Results and Discussion

Electronic Structure of Picolyl Chlorides. The electron densities of picolyl chlorides in the ground and first excited and triplet states are calculated by SCF-MO-CI PPP method and are summarized in Table 2 and 3. The electron density at methylene carbon in the ground state increases in the order of 2-PC<3-PC<4-PC mainly due to the inductive and resonance effect of electronegative nitrogen atom in the ring. The electron density at methylene carbon in the first excited singlet and triplet states is much lower than that of the ground state and the value is lower in the excited singlet state than the triplet state. The order is 2-PC<3-PC<4-PC in the excited singlet state, the same as that of the ground state but 3-PC<2-PC<4-PC in the triplet state. The electron density at nitrogen atom is in the order of $S_0<S_1<T_1$ for 2-and 3-PC but $T_1<S_0<S_1$ for 4-PC.

The $^1(n, \pi^*)$ band is buried under the strong $^1(\pi,\pi^*)$ band in the UV spectra of picolyl chlorides as in the case of pyridine. The $^1(\pi,\pi^*)$ transition energy calculated by SCF-MO-CI PPP method is in good agreement with the experimental value for 2- and 3-PC but the difference between experimental and calculated value is significant in 4-PC, as shown in Table 4.

TABLE 2: Electron Densities of Ground State Picolyl Chlorides



	2-PC	2-PC	4-PC
1	1.315741	1.215484	1.271516
2	0.691583	0.995260	0.892938
3	1.105634	0.796865	1.108963
4	0.948337	1.051144	0.739649
5	1.060793	1.003581	1.108960
6	0.894213	0.948003	0.892935
7	1.250546	1.251833	1.253245

Solvolysis of Picolyl Chlorides. Picolyl chlorides undergo substitution reaction with nucleophiles such as pyridine, alkyl amines, and alkoxides. The reaction rate is too fast to study when an alkoxide is used as a nucleophile. Since pyridine ring itself of picolyl chlorides can react as a nucleophile, weaker nucleophiles than pyridine cannot be used in the solvolytic study of picolyl chlorides.

Picolyl chlorides are solvolyzed in pyridine solvent. The reaction rates are measured by monitoring the intensity of methylene proton peak in the picolyl chlorides nmr spectra. The methylene proton chemical shift at 4.5 ppm is about 0.5 ppm downfield or upfield shifted as the chlorine atom is replaced by pyridine ring. The invariant intensity of pyridine proton peaks are used as a standard. Thus measured rate constants are summarized in Table 5 and the activation parameters are calculated and shown in Table 6.

The characteristics of S_N2 reactions are obvious as shown by the relatively small activation enthalpies of 14–17 Kcal/mole and large activation entropies of $-32\sim-25$ eu(7). Since the leaving group, solvent, and steric hindrance are all identical in the solvolysis of 2–, 3–, and 4–PC, the electron density at the reaction center, methylene carbon, is expected

TABLE 4: Lowest (π, π^*) Transition Engergy of Picolyl Chlorides

Compds.	Experimental	Calculated	
	E_s(kcal/mole)	E_s(kcal/mole)	E_T(kcal/mole)
2-PC	105	110	75.1
3-PC	105	109	74.4
4-PC	108	126	80.5

TABLE 5: Rate Constants for the Reaction of Picolyl Chlorides in Pyridine

Compds.	$k(\times10^{-5}sec^{-1})$		
	25°C	38°C	50°C
2-PC	2.11	5.41	14.9
3-PC	1.96	4.31	13.4
4-PC	0.755	3.51	7.84

TABLE 6: Activation Parameters for the Reaction of Picolyl Chlorides in Pyridine

Compds.	$H^{\neq}$(kcal/mole)^a	$S^{\neq}$(e,u)^b	E^a(kcal/mole)
2-PC	14.2	−32.3	14.8
3-PC	14.1	−32.8	14.7
4-PC	17.1	−24.7	17.6

^{a,b}at 298 °K.

TABLE 3: Electron Densities of Excited State Picolyl Chlorides

	2-PC		3-PC		4-PC	
	Singlet	Triplet	Singlet	Triplet	Singlet	Triplet
1	1.39743	1.43061	1.39044	1.41738	1.27339	1.26879
2	0.63931	0.60585	0.99213	0.99302	0.97770	0.93113
3	1.02179	0.94280	0.66041	0.62782	1.02662	1.06797
4	1.16673	1.04946	1.17748	1.29349	0.77686	0.75280
5	0.88876	0.98642	1.01485	1.00236	1.02662	1.06797
6	0.96241	1.03491	0.84654	0.72928	0.97770	0.93113
7	1.21718	1.23563	1.21735	1.23071	1.22069	1.24416

to be the controlling factor. The order of the electron density at the methylene carbon is 2-PC<3-PC<4-PC as is the opposite of the order of the substitution rate constants supporting the foregoing arguments.

Photosolvolysis of Picolyl Chlorides. In the photosolvolysis of picolyl chlorides, *sec*- and *t*-butylamine are utilized as nucleophiles instead of pyridine since pyridine and picolyl chlorides have about the same UV absorption characteristics and pyridine solvent will absorb most of the UV light of 254 nm if pyridine is used as a nucleophilic solvent.

The photosolvolysis products are identified by nmr spectral analyses. The same nucleophilic substitution products were obtained in the photo- and thermal solvolysis of picolyl chlorides in alkyl amines. The products such as picoline, 1,2-dipyridyl ethane, etc., which are expected from homolysis of C-Cl bond in picolyl chlorides on irradiation, are not detected. Therefore, the photosubstitution reaction of picolyl chlorides with alkyl amines undergoes through C-Cl bond heterolysis only in contrast to benzyl chlorides which give both homolysis and heterolysis products on direct irradiation (3).

The quantum yield of photosubstitution reaction of picolyl chlorides with *t*-butylamine is shown in Table 7 along with the thermal reaction rate constants. The rate of thermal reaction is faster than that with pyridine nucleophile since *t*-butylamine is stronger nucleophile than pyridine but the order is the same 2-PC>3-PC>4-PC. The reaction rate is faster in the photosolvolysis than in the thermal reaction. The results are consistent with the lower electron densities at methylene carbon atom in the first excited singlet and triplet states compared to that of the ground state. However, the order of the quantum yield is 3-PC>2-PC>4-PC which is quite different from the rate order of the thermal reaction.

The controlling factor for the rate of photosubstitution reaction will be again the electron density of methylene carbon atom since the photosubstitution occurs through heterolysis of C-Cl bond. The order of the electron density at methylene carbon in the first excited singlet state is 2-Pc< 3-PC<4-PC, the same as that of the ground state but the order is 3-PC<2-PC<4-PC in the triplet state. Thus the photosubstitution reaction of picolyl chlorides with *t*-butylamine seems to occur through the triplet state of picolyl chlorides. The electron density at methylene carbon is much lower in the first excited singlet state than the triplet state but the short lifetime of the first excited singlet state and the long lifetime of the triplet state make the reaction to go through the triplet state. Piperylene does not quench the reaction efficiently and no sensitization study is carried out since the triplet energy of picolyl chlorides is quite high (~85 kcal/mole) (9) and no sensitizer with this high triplet energy and right UV absorption characteristics could be found. The multiplicity of the reactive state in the photosubstitution reaction of picoly chlorides is, therefore, not clearly determined even though the faster rate than the thermal reaction, the rate order of 3-PC>2-PC>4-PC, and the long lieftime of the triplet state support the triplet mechanism.

TABLE 7: Relative Quantum Yields for the Photochemical Reaction and Rate Constants for the Thermal Reaction of Picolyl Chlorides in *t*-Butylamine at 25 °C

Compds.	Relative *Q.Y.*	$k(\times 10^{-5}\ \mathrm{sec}^{-1})$
2-PC	0.73	6.48
3-PC	1	4.04
4-PC	0.50	2.60

References

(1) E. Havinga, R. O de Jongh, and W. Dorst, *Rec. Trav. Chim.*, **75**, 378 (1956).
(2) H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, **85**, 915 (1963).
(3) S. J. Cristol and T. H. Bindel, *J. Org. Chem.* **45**, 951 (1980).
(4) D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, "Purification of Laboratory Chemicals", Pergamon Press, London, 1966.
(5) C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.*, **A235**, 518 (1956).
(6) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21**, 466 and 767 (1953).
(7) J. A. Pople, *Trans. Faraday Soc.*, **49**, 1375 (1953).
(8) N. Mataga and K. Nishimoto, *Z. Phys. Chem.* (*Frankfurt am Main*), **13**, 140 (1957).
(9) S. L. Murov, "Handbook of Photochemistry," p. 35, Marcel Dekker, Inc., New York. 1973.