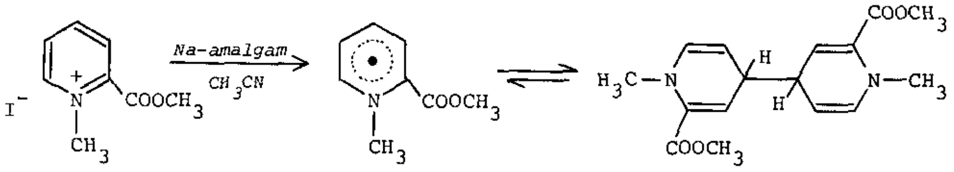
HETEROCYCLES, Vol 15, No 2, 1981

AN ELECTRON SPIN RESONANCE STUDY ON THE PROPERTIES OF 1-METHYL-2-METHOXYCARBONYLPYRIDINYL AND THE DIMER

Yusaku Ikegami*, Masako Sawayanagi, and Shozo Kubota
Chemical Research Institute of Non-Aqueous Solutions
Tohoku University, Katahira, Sendai 980, Japan

The electron spin resonance study of the 1-methyl-2-methoxycarbonylpyridinyl radical, which is in equilibrium with a large amount of the dimer in solution, elucidated the hyperfine splitting constants, the remarkable dependence of the signal intensity on temperature, and the line-broadening with a rise in temperature above 0°C. The activation energy for the monomer-dimer interconversion was evaluated to be 9.4 kcal/mol in 2-methyltetrahydrofuran. Light irradiation of the dimer in 2-methyltetrahydrofuran at 77 K led to an appearance of the triplet spectrum with $D = 0.0155\ \mathrm{cm}^{-1}$ due to the radical pair generated by photochemical dissociation of the dimer. Further irradiation of the solution altered gradually the line shape.

The preparation of 1-methyl-2-methoxycarbonylpyridinyl ($I^{\cdot}$), the one electron reduction product of the corresponding pyridinium ion, was first attempted in 1972 and some properties of the radical solution were reported.[1] The properties, however, were at some variance with those expected in both absorption spectrum and chemistry. Basing upon the recent advance in the chemistry of pyridinyl radicals,[2] a thorough investigation for this radical has been carried out on all matters pertaining to the preparation, absorption spectroscopy of the solutions and thin film of the radical, esr spectroscopy, and photochemical behaviors, as well as electrochemical reduction of the precursor cation. The results were recently summarized with a chemical understanding that a small amount of $I^{\cdot}$ is in equilibrium with the covalently bonded dimer (I-I).[3] This paper deals with the results obtained in the course of our esr study on these species. Some other experimental results will also be mentioned.



($I^{\cdot}$)   (I-I)

Results and Discussion

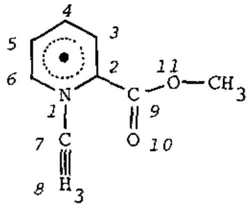
Preparation and Purification of I-I: Treatment of 1-methyl-2-methoxycarbonylpyridinium (I^+) iodide in acetonitrile with 2.5 % sodium amalgam in the absence of air at 0°C for about 40 min afforded a colorless solution. Evaporation of the solvent and extraction with 2-methyltetrahydrofuran (MTHF), followed by the distillation onto a 77 K surface, gave a blue film of the radical. Dissolution of the blue film or an elevation of the temperature[4] led to a loss of its color. The colorless solution showed the following properties. (1) The absorption spectrum has the maxima at 245 ($\varepsilon = 10000$ as I-I) and 332 nm (2000) in acetonitrile and the feature is in contrast with those of 1-methyl-4-methoxycarbonylpyridinyls. (2) A weak esr signal with well-resolved hyperfine structure is observed at room temperature even for the highly concentrated solution in either acetonitrile or MTHF. (3) The solution reacts with 1,1'-dimethyl-4,4'-bipyridinium dichloride in acetonitrile to form the cation radical, which shows the strong esr signal and the characteristic absorption spectrum with maximum at 605 nm ($\varepsilon = 13000$).[3] And, (4) 1-alkyl-4-methoxycarbonylpyridinium ions are also reduced producing the corresponding neutral radicals. These results can be interpreted in terms of the equilibrium between the monomer ($I^{\cdot}$) and the dimer (I-I) in solution. With the association constant larger than $3 \times 10^4\ mol^{-1} \cdot dm^3$,[3] the radical is found mainly in the form of dimer. The structure of I-I given by some reasons is supported by the pmr measurement for the concentrated solution.[5]

Hyperfine Structure of the Esr Spectrum: The esr spectrum of $I^{\cdot}$ in MTHF is shown in Fig. 1. The well-resolved hyperfine structure is usually observed even for a highly concentrated solution such as $3 \times 10^{-2}\ mol/dm^3$. This indicates that the exchange process in the equilibrium is very slow, compared with the time scale in the esr experiment, and that the radical concentration is quite low. Hyperfine structure of the spectrum is analyzed with seven splitting constants on computer simulation. The constants in some conditions are listed in Table 1, in which the dependences of the constants on temperature and on solvent are clearly pointed out.

Table 1. Hyperfine Splitting Constants and Calculated Spin Densities of I$^{\cdot}$

Position (Coupled atoms)		Splitting constants, a_i (G)									Calcd. ρ_i $^{a)}$
		In acetonitrile				In MTHF					
		-20°C	0°	19°	40°	-40°	-20°	0°	20°	40°	
1-	(1N)	6.60	6.44	6.58	6.65	6.39	6.45	6.49	6.55	6.50	0.1275
3- or 5-	(1H)	1.33	1.37	1.40	1.46	1.36	1.43	1.49	1.54	1.58	-0.0603
4-	(1H)	6.26	6.26	6.28	6.37	6.19	6.19	6.21	6.30	6.31	0.2203
5- or 3-	(1H)	0.96	0.97	0.94	0.93	1.03	1.05	1.08	1.11	1.11	-0.0083
6-	(1H)	2.69	2.58	2.54	2.45	2.58	2.50	2.39	2.36	2.28	0.1543
NCH_3	(3H)	5.74	5.66	5.64	5.52	5.77	5.73	5.64	5.67	5.62	
OCH_3	(3H)	0.96	0.95	0.94	0.93	0.94	0.93	0.91	0.90	0.89	

a) Parameters for the McLachlan Calculation:



$\alpha_1 = \alpha + 2\beta$, $\alpha_6 = \alpha + 0.2\beta$,
$\alpha_7 = \alpha - 0.1\beta$, $\alpha_8 = \alpha - 0.5\beta$,
$\alpha_{10} = \alpha + 2\beta$, $\alpha_{11} = \alpha + 2\beta$,
$\beta_{1,7} = 0.7\beta$, $\beta_{7,8} = 2.5\beta$,
$\beta_{2,9} = 0.9\beta$, $\beta_{9,10} = 1.4\beta$,
$\beta_{9,11} = 0.7\beta$, $\lambda = 1.2$.

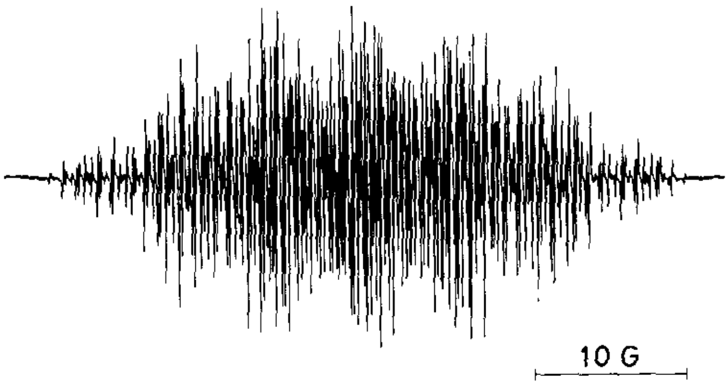


Fig. 1. ESR spectrum of I$^{\cdot}$ in MTHF at 10°C, $c = 1.19 \times 10^{-3}$ mol/dm^3 as I-I.

The assignments were given according to the type of splitting, with a study on the 1-trideuteriomethylpyridinyl radical,[1] and by comparing the constants with the calculated spin densities. No good agreement between the observed and calculated spin densities has been obtained. However, the spin distribution (Table 1) calculated by the McLachlan procedure, adopting a conjugation model for the methyl group, permits the tentative assignments for the splitting constants.[6]

Temperature Dependences of Line Intensity and Line Width: Dependence of the esr-line intensity for I-I in MTHF on temperature is shown in Fig. 2(a), in which the intensity (A') is relative to that of the reference signal of Mn^{2+} ion. The remarkable dependence is readily ascribed to the shift of the equilibrium between I$^{\cdot}$ and I-I on temperature. If the rapid process in the equilibrium occurs at temperatures available for esr experiments, broadening of the hyperfine lines with a rise in temperature would be observed. Fig. 2(b) shows the temperature dependence of line width measured for the solution of I-I in MTHF.

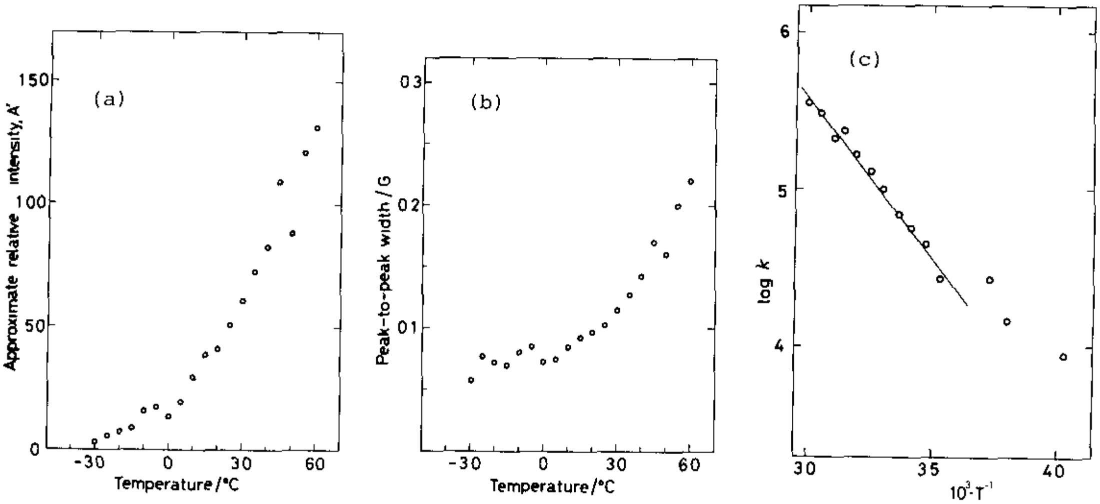


Fig. 2. Temperature dependences of (a) the line intensity (A' in arbitrary unit) and (b) the peak-to-peak line width (ΔH_{pp}) in the esr spectrum of I$^\bullet$. (c) A plot of log k versus the reciprocal of the temperature. The spectra were measured in MTHF at a concentration of 1.17×10^{-3} mol/dm^3 of I-I.

Using the relationship between the line width ($\Gamma = \Delta H_{pp}\sqrt{3}/2$) and the mean lifetime of the radical in the limit of slow interconversion (Eq. 1)[7]

$$\Gamma = \Gamma_0 + 1/2\tau\gamma_e \qquad (1)$$

where Γ_0 is the line width in gauss in the absence of interconversion, 2τ the mean lifetime of the radical, and γ_e the gyromagnetic ratio of electron, the rate constant, k, for spin exchange ($= 1/\tau$) was obtained. Γ_0 was evaluated from the widths at temperatures lower than -10°C to be 65.0 mG. A plot of log k versus $1/T$ gave a least-squares line (Fig. 2(c)) for a temperature range 10—60°C, $\log k = 11.75 - 2054T^{-1}$, from which the arrhenius relation yielded an activation energy of 9.4 ± 0.3 kcal/mol. A similar treatment of the data for the line width in acetonitrile led to an activation energy of 7.7 ± 0.4 kcal/mol with $\Gamma_0 = 76.2$ mG and $\log k = 11.06 - 1677T^{-1}$. The second-order rate constant for dimerization evaluated from the $1/\tau$ value and by assuming the radical concentration given by the equilibrium constant ($= 4 \times 10^5$ mol$^{-1}\cdot$dm^3)[3] is larger than 1×10^9 mol^{-1}dm^{3}s^{-1} at room temperature, which represents a diffusion controlled reaction.

Photochemical Dissociation of I-I and Triplet Spectrum of the Radical Pair: As pointed out in Fig. 2(a), the esr signal of the radical solution weakens with a lowering of temperature and disappears almost completely at around -50°C. Irradiation of the solution with visible light caused an increase or a reappearance of the signal with hyperfine structure, showing the homolytic dissociation of I-I to form the radical. At 0°C, the change in the intensity was little on irradiation; in the temperature range 0— - 70°C, the lower the temperature, the larger the rate of increase of the intensity. The rate of change in line intensity was very rapid for both turning on and turning off the light in MTHF, but a remarkable dependence of the rate of recombination on temperature was observed at temperatures lower than -30°C. This rate would be affected by the viscosity of solvent and the further study is in progress. The photodissociation of I-I occurred with light of the range 330—400 nm. This wavelengths range corresponds to an absorption band with the maximum at 332 nm, which is identified as a sigma-pi—sigma-pi* transition in the dimer.[4]

Irradiation of the MTHF glass containing I-I at 77 K with light of wavelengths between 400 and 470 nm led to the appearance of a strong triplet signal in the esr spectrum. The $\Delta M = 2$ transition was also observed at 1610 G. Long irradiation or irradiation with shorter wavelengths caused some change in the shape of the triplet spectrum. A typical result is shown in Fig. 3. The spectra of VY-46(a), VY-46(b), and VY-44(a) in Fig. 3 yielded the zero-field parameters, $D = 0.0155\ \mathrm{cm}^{-1}$ and $E \sim 0$, with $2D = 332$ G. This D value corresponds to the spin-spin interaction for an

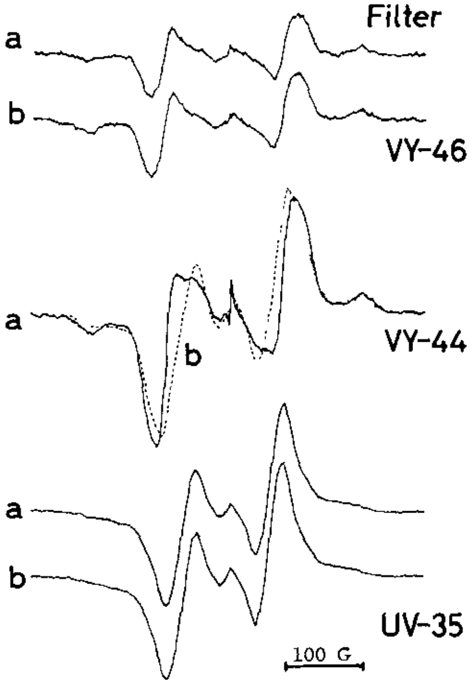


Fig. 3. Triplet spectra of the radical pair generated from I-I after (a) 5 min and (b) 30 min irradiation with a 500 W xenon lamp using Toshiba filters.

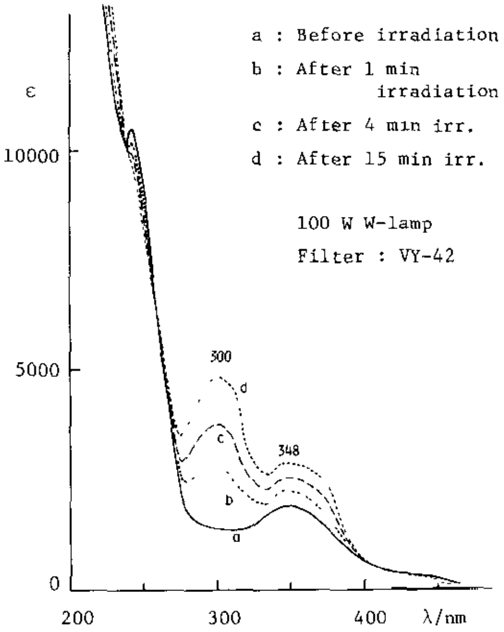


Fig. 4. Spectral change of the solution of I-I in MTHF on light irradiation at 77 K.

average separation of 5.5 Å in the radical pair. Lines in both spectra of UV-35, as well as those of VY-44(b), are comparatively broad, though the *D* value (= 0.0146 cm^{-1}) are similar to the above. Such a change in the spectral shape is ascribed to that the absorption of light in the 400 nm region by the radical comes in effect to loosen the difinite structure of the radical pair in a solvent cage. The change of the absorption spectrum of I-I in MTHF at 77 K on irradiation is shown in Fig. 4. The gradual increase of the bands at 300 and 348 nm clearly demonstrates the generation of the 1-methyl-2-methoxycarbonylpyridinyl radical.

Conclusion: The equilibrium between the radical I$^{\cdot}$ and the dimer I-I and the photodissociation of I-I have been established. Such a radical is referred to intermediate stability pyridinyl radicals and the properties would be exceedingly useful to understand the properties of both stable and unstable pyridinyl radicals.

The present work was carried out as a part of the joint research on 1-alkyl-2-methoxycarbonylpyridinyls with Professor E. M. Kosower and his co-workers, to whom the authors are greatly indebted for their helpful advice. The work was partially supported by a Grant-in-Aid for Scientific Research No. 343002 from the Ministry of Education, Science and Culture.

References and Notes

1. H. Watanabe, Y. Ikegami, and S. Seto, Chem. Lett., 1972, 1107.
2. The subject of pyridinyl radicals is reviewed by E. M. Kosower, in 'Free Radicals in Biology', Vol. 2, Chap. 1, W. A. Pryor ed., Academic Press, New York, 1976.
3. J. Hermolin, M. Levin, Y. Ikegami, M. Sawayanagi, and E. M. Kosower, J. Am. Chem. Soc., submitted.
4. J. Hermolin, M. Levin, and E. M. Kosower, J. Am. Chem. Soc., submitted.
5. Y. Ikegami and M. Sawayanagi, unpublished results.
6. A remarkable effect of the addition of $LiClO_4$ to the solution of I$^{\cdot}$ in acetonitrile has been observed on the hyperfine structure, the splitting constants in this solvent containing $LiClO_4$ (0.4 mol/dm^3) being 5.65(1N), 6.20(1H), 5.63(3H), 2.92(1H), 1.06(1H), 1.07(3H), and 0.67 G(1H) in order as in Table 1 at 20°C.[5]
7. J. E. Wertz and J. R. Bolton, 'Electron Spin Resonance, Elementary Theory and Practical Applications', McGraw-Hill, New York, 1972, pp. 198-204.

Received, 8th September, 1980