Electron Spin Resonance Study on Photoinduced Changes of the Radicals Produced in Methyl Isocyanate Solid Irradiated with γ-Rays

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Free radicals in the γ-irradiated solid of methyl isocyanate at −196°C have been studied by electron spin resonance (ESR) at $-196\sim-100$°C. An oriented solid of methyl isocyanate was prepared by solidification of methyl isocyanate around an aluminum rod under cooling. The original radical and trapped electron produced by γ-irradiation were recorded at −196°C in the dark. The original radical produced in the oriented solid gave a resonance pattern consisting of a triplet of triplets and was assigned to $\cdot CH_2NCO$ radical. This was converted completely into a new radical on irradiation with visible light for 90 min. The new resonance pattern consists of a triplet of triplets whose nitrogen and proton splitting constants are 20.0 and 87.4 gauss, respectively. The nitrogen hyperfine splitting was anisotropic and the proton splitting constant agreed with that of methylene imino radical ($H_2C{=}N\cdot$). The new radical was assigned to methylene imino radical. The resonance pattern of $\cdot CH_2$-NCO radical was restored when the temperature was raised up to −120°C. The mutual conversion between the two radicals by visible light and heat was concluded to be a decomposition of $\cdot CH_2NCO$ into $H_2C{=}N\cdot$ and CO, and a recombination of these two moieties.

Recently, several ESR studies on reversible changes of free radicals on irradiation of light and heating have been reported on allylic radical[1] in γ-irradiated polyethylene, isobutyl radical,[2] ethoxy radical,[3] and deuterated acetonitrile anion radical.[4] The photochemical changes of allylic and isobutyl radicals were attributed to an intramolecular transfer of hydrogen. On the other hand, the changes of ethoxy radical and deuterated acetonitrile anion radical were suggested to be decomposition and recombination reactions of the radicals.

The radical produced by γ-irradiation of methyl isocyanate at −196°C has been reported by Chung and Williams.[5] The electron spin resonance (ESR) spectrum was recorded at −196°C after the subsequent irradiation of visible light for a short period and ascribed to $\cdot CH_2NCO$ radical. They used the irradiation of visible light only for the purpose of obtaining a more symmetrical spectrum than that obtained in the dark. A slight orientation effect of the specimen was also noted by them. The change of the radical on irradiation of light and heating, however, has not so far been reported.

The object of this work is to study both the photochemical and thermal changes of the radical in γ-irradiated methyl isocyanate solid by ESR spectroscopy. The radical produced by γ-irradiation and the subsequent exposure to visible light are identified with the aid of the anisotropy of the spectrum and the deuteration of methyl isocyanate. The anisotropy is also examined by use of the oriented solid method which has been found to be useful for ESR measurement of vinyl acetate[6] and isocyanic acid,[7] whose melting points are too low for the preparation of single crystals.

Experimental

Methyl isocyanate (guaranteed reagent grade, Tokyo Chemical Industry Company Ltd.) was purified by vacuum distillation. Deuterated methyl isocyanate (CD_3NCO) was prepared in the following manner.[8] Deuterated acetyl chloride (CD_3COCl) was obtained by heating deuterated acetic acid (CD_3COOD) (degree of deuteration=99%, 20 g) with thionyl chloride under reflux. Sodium azide (24 g) dissolved in isoamyl ether (150 g) was added dropwise to the deuterated acetyl chloride, resulting in deuterated acetyl azide (CD_3-CON_3) which was converted into deuterated methyl isocyanate by heating; Total yield=55.0%. The resulting deuterated methyl isocyanate was purified by gas chromatographic fractionation, using a 1 m column of Carbowax 1500. The degree of deuteration was determined as 98.5% with a Hitachi RMU-6 mass spectrometer.

An oriented solid of methyl isocyanate was prepared according to a procedure similar to that used for the preparation of an oriented solid of vinyl acetate.[6] Methyl isocyanate was solidified around an aluminum rod in a glass tube by cooling with liquid nitrogen and was irradiated with ^{60}Co γ-rays (8×10^5—8×10^6 rad) at −196°C.

After γ-ray irradiation, the solidified methyl isocyanate was cleft radially into several pieces, one of which was inserted in a crack of Teflon tube so as to hold the longitudinal axis of the piece, *i.e.* the axis of the mark of aluminum rod, horizontally. The angle between the longitudinal axis of the piece and the direction of the DC magnetic field is referred to as "orientation-angle." Orientation-angle 0 and 90° indicate the axes parallel and perpendicular, respectively, to the magnetic field. The ESR measurement was carried out using a Varian V-4502 X-band spectrometer with 100 KHz field modulation at several different temperatures between

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[1] S. Ohnishi, S. Sugimoto, and I. Nitta, *J. Chem. Phys.*, **39**, 2647 (1963).

[2] M. Iwasaki and K. Toriyama, *ibid.*, **46**, 2852 (1967).

[3] Quoted in a paper by V. V. Voevosdky, The 4th International Symposium on Free Radical Stabilization, B–V–1, 1959.

[4] K. Takeda and F. Williams, *J. Phys. Chem.*, **74**, 4007 (1970).

[5] Y. J. Chung and F. Williams, *ibid.*, **75**, 1893 (1971).

[6] H. Hirai and M. Fujiwara, *Nippon Kagaku Kaishi*, **1972**, 986.

[7] H. Hirai and M. Fujiwara, This Bulletin, to be published.

[8] G. Schroter, *Ber.*, **B-42**, 3357 (1909).

-196 and -100°C. The method described above is referred to as the oriented solid method.

The γ-irradiated solid of methyl isocyanate was exposed to visible light (wave lengths$>$4000 Å) from an Ushio Denki HB 500/B high pressure mercury lamp in a transparent quartz Dewar vessel at -196°C, using a Dow Corning CS-3-75 filter.

Results

γ-Irradiated Methyl Isocyanate in the Dark. Figure 1 shows the ESR spectra of methyl isocyanate and deuterated methyl isocyanate irradiated with γ-rays (1×10^6 rad) and recorded at -196°C in the dark in a Spectrosil tube. Spectra 1a and 1b correspond to methyl isocyanate and deuterated methyl isocyanate, respectively. No changes in the pattern occurred when the Spectrosil tube was rotated about its longitudinal tube axis in the dc magnetic field. The spectra were unsymmetrical because of the overlapping of a singlet at the center of the spectra.

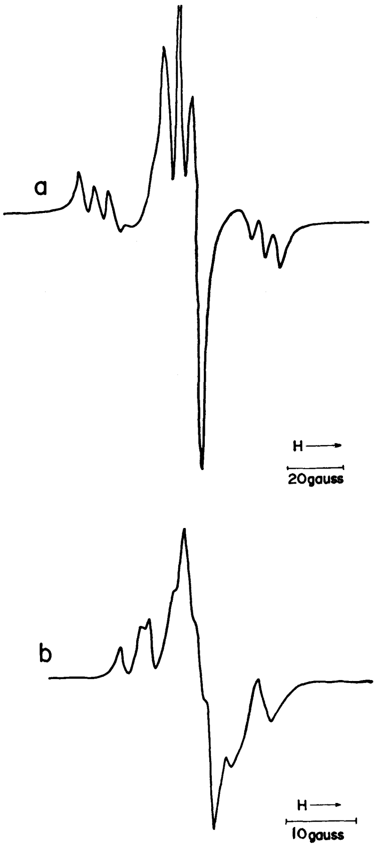

Fig. 1. ESR spectra of methyl isocyanate (a) and deuterated methyl isocyanate (b) irradiated with γ-rays (1×10^6 rad) at -196°C in a Spectrosil tube and measured in the dark.

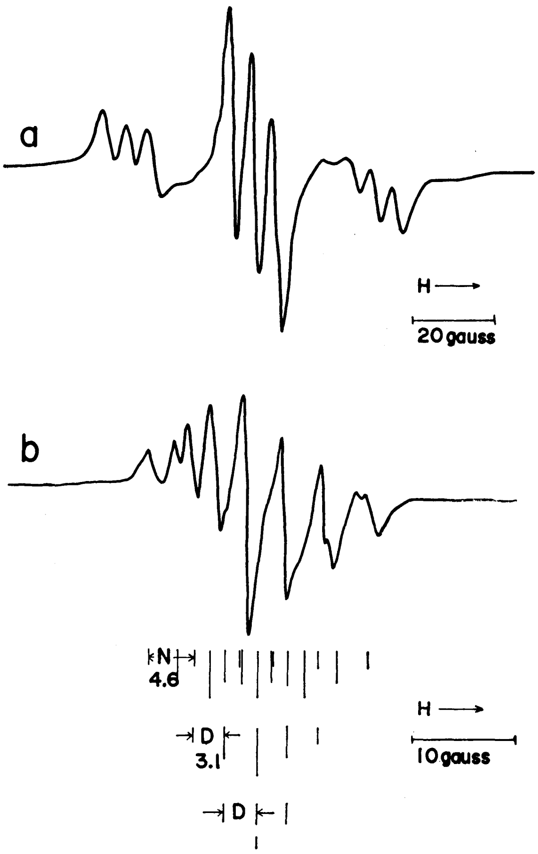

Fig. 2. ESR spectra of methyl isocyanate (a) and deuterated methyl isocyanate (b) irradiated with γ-rays and exposed subsequently to visible light for 1 min.

γ-Irradiated Methyl Isocyanate Exposed to Visible Light for a Short Period. The γ-irradiated methyl isocyanate and deuterated methyl isocyanate exposed subsequently to visible light for 1 min gave spectra 2a and 2b, respectively. Spectrum 2a consists of a set of nine lines which is grouped into a triplet of triplets. Spectrum 2b consists of seven lines with a relative intensity ratio of about 1: 3: 5: 9: 5: 3: 1, the line splitting being 3.5 gauss. The singlet centered at $g=2.002\pm0.001$ disappeared not only on subsequent exposure to visible light for 1 min but also on the storage in the dark at -196°C for a long period (20 hr). This singlet must be the absorption of trapped electron, since its behavior on irradiation of light and its g-value are analogous to those of the trapped electron.[9]

Theoretical intensity ratios of spectrum 2b whose nitrogen and deuteron splitting constants are 4.6 and 3.1 gauss, respectively, are reconstructed as shown at the bottom of Fig. 2. The line splitting, 3.1 gauss, corresponds to 1/6.65 of the proton splitting at orientation-angle 0°. The intensity ratios of the observed line agrees with theoretical ones.

Figure 3 shows the ESR spectra of the γ-irradiated oriented solid exposed subsequently to visible light for 1 min. The oriented solid method gives the anisotropic spectra when the specimen is rotated in the magnetic field keeping the longitudinal axis horizontal; the outer components of the spectra were anisotropic, while the three central lines were isotropic. The spectrum at orientation-angle 0° (Fig. 3a) consists of a triplet of triplets with a relative integral intensity ratio of 1: 2: 1. The larger triplet and the well-defined 1: 1: 1 triplet splittings were 20.6 and 4.6 gauss, respectively, at orientation-angle 0°. The larger triplet splitting at orientation-angle 45° and 90° could not

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[9] J. Lin, K. Tsuji, and F. Williams, *J. Amer. Chem. Soc.*, **90**, 2766 (1968).

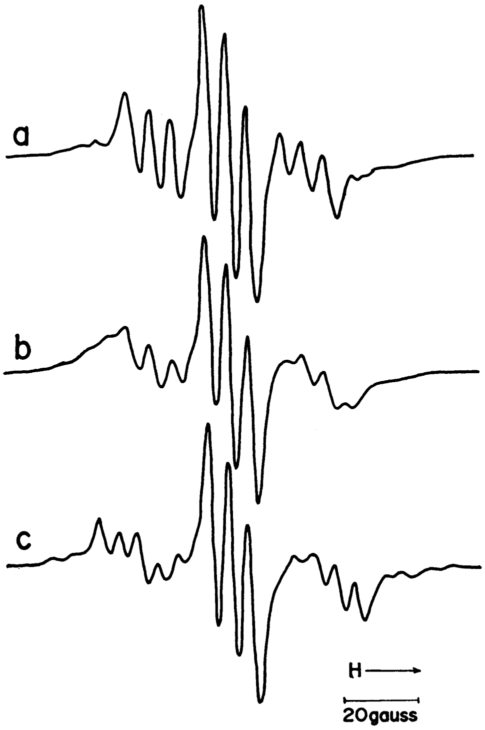

Fig. 3. ESR spectra of oriented solid of methyl isocyanate irradiated with γ-rays and exposed subsequently to visible light with orientation-angles 0° (a), 45° (b), and 90° (c).

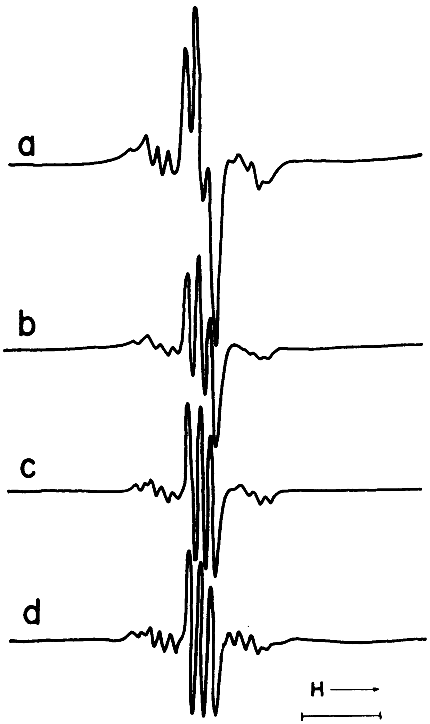

Fig. 4. ESR spectra of methyl isocyanate irradiated with γ-rays and measured at various temperatures; -196°C (a), -180°C (b), -150°C (c), and -120°C (d).

be determined because of broadening of the outer components, while the well-defined triplet splitting of the central components was 4.6 gauss. Elevation of temperature to about -100°C gave no changes in shape except that the singlet disappeared above -180°C as shown in Fig. 4. These results indicate that γ-irradiation of methylisocyanate solid gives only one species of radical, which is hereinafter referred to as Radical **1**.

γ-Irradiated Methyl Isocyanate Exposed to Visible Light for a Long Period. On continuing the irradiation of visible light to the γ-irradiation specimen, a new resonance pattern appeared gradually, accompanied by the disappearance of the original pattern, the changes being completed within 90 min (Fig. 5). The new resonance pattern shown in Fig. 5c was found to consist of a triplet of triplets with a relative integral intensity ratio 1 : 2 : 1. The main triplet splitting was 87.4 gauss, which agreed with that of the proton splitting constant of methylene imino free radical.[10] Each line of the main triplet was split into a secondary triplet whose splitting constant was 20.0 gauss. It was observed that the outer lines of each secondary triplet were weak and unsymmetrical, indicating that the hyperfine interaction responsible for this splitting is anisotropic. The new radical produced by the irradiation of visible light is referred to as Radical **2**. The concentration of Radical **1** obtained with spectrum 5a was almost equal to that of Radical **2** obtained with spectrum 5c.

Elevation of temperature of the γ-irradiated specimen exposed subsequently to visible light for 90 min showed a remarkable change in which the resonance pattern

Fig. 5. The changes of ESR spectra of methyl isocyanate irradiated with γ-rays and exposed subsequently to visible light for 5 min (a), 30 min (b), and 90 min (c).

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10) E. L. Cochran, F. J. Adrian, and V. A. Bowers, *J. Chem. Phys.*, **36**, 1938 (1962).

of Radical **1** was regenerated, accompanied by the decrease of the pattern of Radical **2** (Fig. 6). The change was completed at −120°C. When the γ-irradiated specimen was warmed at about −120°C without the irradiation of visible light and subsequently exposed to visible light at −196°C for 90 min, the resonance pattern of Radical **2** appeared. This indicates that the mutual change between the two radiacls by visible light and heat was a reversible conversion of radical.

Fig. 6. The changes of ESR spectra of methyl isocyanate irradiated with γ-rays and exposed subsequently to visible light for 90 minutes at various temperatures; −196°C (a), −150°C (b), and −120°C (c).

The resonance pattern of deuterated methyl isocyanate also changes with the irradiation of visible light to the spectrum which consists of a quintuple of triplets (Fig. 7). The splitting of the main quintet with intensity ratio 1 : 2 : 3 : 2 : 1 was 13.1 gauss. Each line of the main quintet splits into a secondary triplet whose splitting constant is 20.0 gauss (Fig. 8). The value of this quintet splitting corresponds to 1/6.67 of the main triplet splitting of Radical **2** in methyl isocyanate and is ascribed to deuteron coupling. The secondary triplet splitting remains constant both for methyl isocyanate and for deuterated methyl isocyanate and is assigned to nitrogen coupling. Accordingly, the main triplet and the secondary triplet splitting of Radical **2** can be derived from the two protons and nitrogen coupling, respectively.

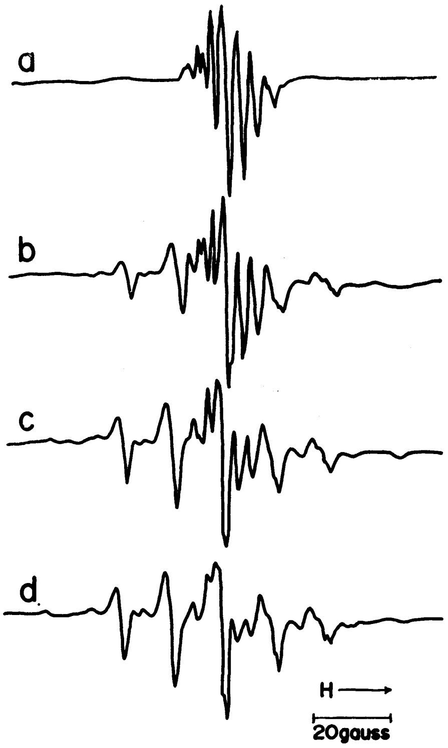

Fig. 7. The changes of ESR spectra of deuterated methyl isocyanate irradiated with γ-rays and exposed subsequently to visible light for 1 min. (a), 5 min (b), 30 min (c), and 90 min (d).

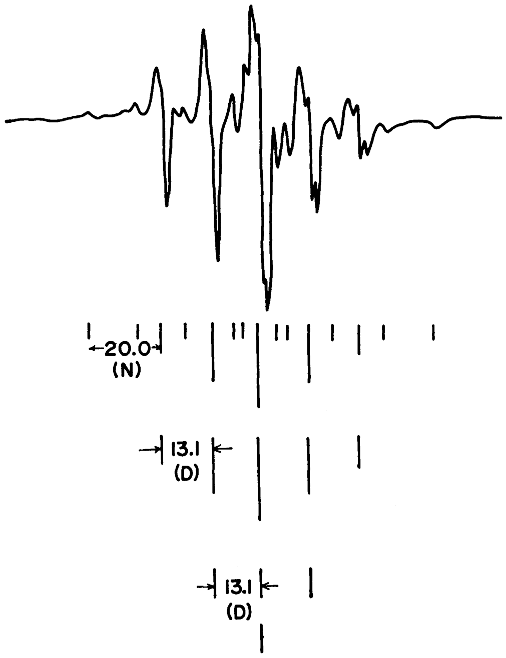

Fig. 8. ESR spectrum of deuterated methyl isocyanate irradiated with γ-rays and exposed to visible light for 90 min.

Determination of g-*values of Radical 2.* The shape of the ESR lines of deuterated Radical **2** (Fig. 8) clearly shows unsymmetrical absorption lines in the lower magnetic field and absorption lines separated into three lines in the higher magnetic field. The shape was ascribed to the broadening effect of the magnetic anisotropy similar to the case for DĊO radical.[11] The line width between the strong five lines of the deuterated Radical **2** shows that the line broadening is due to the combination of anisotropic *g*-values and hyperfine interactions both with deuteron

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11) F. J. Adrian, E. L. Cochran, and V. A. Bowers, *J. Chem. Phys.* **36**, 1661 (1962).

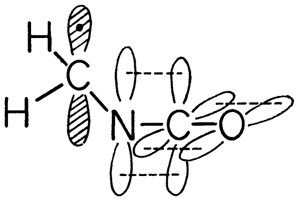
and nitrogen. In the spectra of deuterated Radical **2**, the central line broadening due to the anisotropy of g-value is large compared to the line width due to the other sources such as the anisotropic hyperfine interactions, since the magentic quantum numbers, M_I, both of nitrogen and of deuteron are zero. In this case, the principal g-values could be determined from the central strong line of the deuterated Radical **2**. The high- and low-field peaks of the derivative of the ESR absorption gave g_x and g_z, respectively, while g_y corresponded to the crossover point where the derivative vanished. The results are given in Table 1.

Table 1. Principal components of the g-value for radical **2**

$g_x=2.0038$
$g_y=2.0023$
$g_z=2.0015$

Discussion

Structure of Radical 1. The resonance pattern of spectrum 3a gives us the assignment of Radical **1**. The well-defined 1:1:1 triplet structure (4.6 gauss) is ascribed to the isotropic nitrogen coupling and the larger triplet structure (20.6 gauss) with a relative intensity ratio 1:2:1 to the coupling of the two equivalent protons. The anisotropy of spectra (Fig. 3) suggests that the protons of Radical **1** are α-protons. The outer components of spectra 3b and 3c consisted of many absorption lines due to the coalescence of the ESR absorption lines with different splitting constants caused by the anisotropic hyperfine interaction of α-protons. Accordingly, the nine-line spectrum can be assigned to $\cdot CH_2NCO$ radical. The two equivalent α-protons, as would be the case for a rotating methylene group,[12] give such characteristic hyperfine structures that the central component remains narrower and the outer components become broader. These characteristic structures which are typical of non-oriented specimen are found in spectrum 2a. Consequently, the methylene group of $\cdot CH_2NCO$ radical is assumed to be rotated around the C–N bond and the radical can be represented by the following formula;



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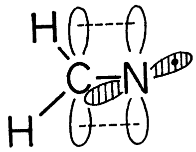
The unpaired electron occupies the carbon 2p orbital. The unpaired electron density on carbon atom ($=\rho_C$) which is estimated to be about 0.8 from the proton splitting may be reasonable, since the 2p orbital occupied by the unpaired electron is rotated around the C–N bond. The fact that the proton splitting is 20.6 gauss was confirmed by the result of deuterated methyl isocyanate; the ESR spectrum consists of fifteen-line, a quintuple of triplets (the bottom of Fig. 2b) and the splitting of quintet component of fifteen-line due to the deuteron coupling is 3.1 gauss, corresponding to 1/6.65 of proton splitting at orientation-angle 0°, while the splitting of triplet component due to the nitrogen coupling equals that of undeuterated specimen.

Structure of Radical 2. The proton splitting of Radical **2** gave the same value as that of methylene imino free radical[10] and the nitrogen splitting was anisotropic (Fig. 5). This suggests that the structure of Radical **2** is analogous to that of methylene imino radical. The unpaired electron of methylene imino radical occupies a nitrogen 2p orbital which is perpendicular to the C–N bond lying in the same plane as the C–H bonds.[10] Thus, three types of the structure might be proposed as shown in Structures **3**, **4**, and **5**;



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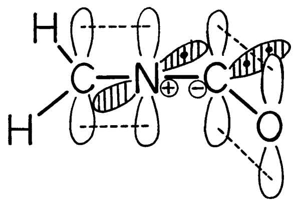

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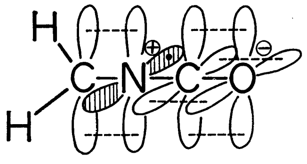

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where Structure **3** is methylene imino radical itself and the radicals with Structures **4** and **5** are isomers of Radical **1**. The unpaired electron of Structure **3** occupies the nitrogen 2p orbital. In Structure **4**, it is located at an antibonding σ-molecular orbital (MO) consisting of sp^2 carbon hybrid orbital and nitrogen 2p orbital. In Structure **5**, it occupies a conjugated orbital consisted of nitrogen 2p orbital and π-orbital of carbonyl group.

The experimental values of nitrogen splitting and unpaired electron density on nitrogen atom ($=\rho_N$) are given by Adrian[13] for HCN$^-$ radical. The unpaired electron occupies an antibonding σ-orbital similar to that of Structure **4** which consists of a sp^2 carbon hybrid orbital and a nitrogen 2p orbital. The observed

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[12] E. L. Cochran, F. J. Adrian, and V. A. Bowers, *ibid.*, **34**, 1161 (1961).

[13] F. J. Adrian, E. L. Cochran, V. A. Bowers, and B. C. Weatherley, *Phys. Rev.*, **17**, 129 (1969).

value of nitrogen splitting (20.0 gauss) agrees with A_1 (20.9 gauss) of HCN^- radical. The value of ρ_N (=0.41) in HCN^- radical, however, is much smaller than that of Structure **3** ($\rho_N=1$). The unpaired electron of Structure **5** may be delocalized in the π-orbital of carbonyl group and ρ_N is estimated to be as large as that of allyl radical.[14] The delocalization of unpaired electron density can not give the large splitting of proton and nitrogen. Thus, Structures **4** and **5** are discarded. On the other hand, Structure **3** is acceptable for the interpretation of the large proton splitting and anisotropic nitrogen splitting. For the methylene imino radical in motion in the hydrogen cyanide matrix at −196°C, the nitrogen splitting has reported to be 11—21 gauss[15] which coincides with the observed value of spectrum 5c. Cochran reported that the nitrogen splitting was 34.4 gauss[10] in rigid argon matrix at 4.2°K. The matrix of methyl isocyanate should not be so rigid as to prohibit the motion of the radical at −196°C. Consequently, Structure **3** is most plausible for the assignment of Radical **2**. The authors had first considered that the mutual conversion between Radicals **1** and **2** was the isomerization between Radical **1** and the radical with Structure **4**, since Radical **1** changed quantitatively into Radical **2** on irradiation with visible light, and Radical **1** was regenerated as the temperature was raised.[16]

The mechanism of mutual conversion between Radicals **1** and **2** may be as follows. The decomposition of Radical **1** into $H_2C{=}N\cdot$ and CO, and the recombination of these two moieties $H_2C{=}N\cdot$ and CO might take place in the neighborhood of each other in the matrix of methyl isocyanate which is so rigid as to stabilize $H_2C{=}N\cdot$ at −120°C. This reaction can be represented by the formula

$$\cdot CH_2NCO \underset{\Delta}{\overset{h\nu}{\rightleftarrows}} H_2C{=}N\cdot + CO$$

The authors wish to thank Dr. Hiroaki Sawai, the University of Tokyo, for his help in preparing deuterated methyl isocyanate.

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[14] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

[15] R. J. Egland and C. R. Symons, *J. Chem. Soc., A*, **1970**, 1326.

[16] The referee's suggestion that ρ_N of Structure **4** is too small to give the proton splitting (87.4 gauss), has been carefully investigated and accepted. The authors wish to thank the referee for his valuable suggestion.