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Photoreaction of *N*-Alkylamides Containing Iron(III) Chloride by Monochromatic Light

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Synopsis. The photolysis of *N*-alkylamides containing $FeCl_3$ using monochromatic light corresponding to the absorption maxima were examined by ESR. Irradiation by 313-nm light resulted mainly in a hydrogen abstraction from the aliphatic carbon adjacent to either CO or NH, whereas 366-nm light produced an acyl radical in larger amounts.

The photoreduction of coordinated metal ions, accompanied by an oxidation of their ligands, is an interesting problem.[1] Recently, we have reported on an ESR study of the photolysis of some *N*-alkylamides containing $FeCl_3$ by UV light irradiation (300—400 nm).[2] We showed that: 1) Some amides gave a mixture of radicals consisting of **a** and **b** or **c** at liquid-nitrogen temperature and 2) amide–$FeCl_3$ complexes gave two absorption maxima in a $CHCl_3$ solution at 312 and 350 nm. Here, we report that the irradiation of amide–$FeCl_3$ complexes with 313-nm light, corresponding to one of the absorption maxima, gave mainly a hydrogen-abstracted radical (**b** or **c**). However, irradiation with 366-nm light, corresponding to another absorption maxima, gave an increased relative molar ratio of the acyl radical **a**.

$RCH_2\dot{C}O$	$RCH_2CONH\dot{C}HR'$	$R\dot{C}HCONHCH_2R'$
a	**b**	**c**

Photoreaction experiments were carried out on eight amides. Here, a typical example is given. The irradiation of the *N*-ethyl-acetamide (**2**)–$FeCl_3$ mixture at 77 K by 313-nm light for 20 min gave the ESR spectrum shown in Fig. 1a. It was analyzed and shown to be a 72/28 mixture of a 1:4:6:4:1 quintet

Table 1. Radicals Generated from Photoirradiated Amide-$FeCl_3$ Mixture and Their Relative Molar Ratio Observed by ESR at 77 K

Amides	313 nm[a] *g*-Value, A_H/mT	(**b** or **c**)/**a**	366 nm[b] *g*-Value, W_{msl}/mT	(**b** or **c**)/**a**
$CH_3CONHCH_3$ **1**	CO-side[c] 2.002, 2.20	31/69	Acetyl 2.001, 1.5	42/58
$CH_3CONHCH_2CH_3$ **2**	NH-side[d] 2.002, 2.05	72/28	Acetyl[d] 2.001, 1.5	48/52
$CH_3CH_2CONHCH_3$ **3**	CO-side[e] 2.002, 2.44	69/31	Propanoyl[e] 2.001, 1.3	50/50
$CH_3CH_2CONHCH_2CH_3$ **4**	f) 2.003, 2.05	59/41	Propanoyl 2.001, 1.3	56/44
$CH_3CH_2CONH(CH_2)_2CH_3$ **5**	CO-side[d],[g] 2.002, 2.42	82/18	Propanoyl[d] 2.001, 1.25	71/29
$CH_3CH_2CONH(CH_2)_5CH_3$ **6**	CO-side[d],[g],[h] 2.002, 2.42	83/17	Propanoyl[d] 2.001, 1.2	80/20
$CH_3(CH_2)_2CONHCH_2CH_3$ **7**	NH-side[g] 2.002, 2.21	69/31	Butanoyl 2.001, 1.5	39/61
$CH_3CH_2CONHCH(CH_3)_2$ **8**	CO-side 2.002, 2.40	95/5	Propanoyl 2.001, 1.5	82/18

a) Irradiation by 313 nm light always generated a small to medium amount of acyl radical together with hydrogen-abstracted radical. Values at the right side of this column are the relative molar ratio of hydrogen-abstracted radical/acyl radical. In the cases of **2**, **5**, and **6**, the numerators contain the contribution from the alkyl radical generated from the acyl radical. "NH-side" refers to the radical $-CONH\dot{C}H-$(**b**), and "CO-side" refers to the radical $-\dot{C}HCONH-$(**c**). Because $A_H{}^\alpha$ is indistinguishable from $A_H{}^\beta$ in every case, both of them are represented by A_H. b) Irradiation by 366 nm light always generated a hydrogen-abstracted radical and an acyl radical. Values at the right side of this column are the relative molar ratios of the hydrogen-abstracted radical/acyl radical. c) Yield of the radicals was very low. d) Also containing the alkyl radical decarbonylated from the acyl radical **a**. e) Also containing $\cdot N{=}CH_2$ ($g=2.002$, $A_H=8.9$ mT) generated from $HN{=}CH_2$.[2,10] f) Undetermined.[11] g) On irradiation by 313 nm light, amides **5**, **6**, and **7** produced the 1 : 4 : 6 : 4 : 1 radicals which we assigned to $-X\dot{C}HCH_3$, not $-X\dot{C}HCH_2-$ (X=NH or CO) which occasionally shows a 1 : 2 : 2 : 2 : 1 quintet,[12] because **5**-d_2 ($CH_3CH_2CONHCD_2CH_2CH_3$) gave a quintet ($g=2.002$, $A_H=2.43$ mT) similar to that of **5**. h) Small amount of $-CH_2\dot{C}HCH_2-$ type radical was also existing.[9]

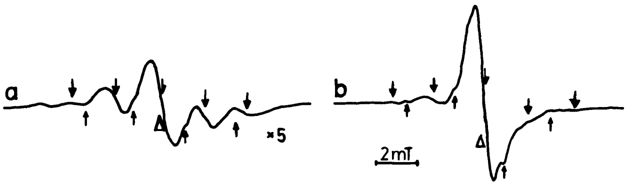

Fig. 1. (a) ESR spectrum of 313nm-irradiated **2**-$FeCl_3$ mixture. (b) ESR spectrum of 366nm-irradiated **2**-$FeCl_3$ mixture. Methyl radical is denoted by an upward arrow, **2a** by a delta, and **2b** by a downward arrow.

(g=2.002, A_H=2.1 mT, **2b**³⁾) and a singlet (g=2.001, W_{msl}=1.5 mT, **2a**⁵⁾),⁶⁾ together with a small amount of the methyl radical generated by decarbonylation from the acetyl radical.²⁾

When the amide (**2**)-$FeCl_3$ mixture was irradiated by 366-nm light, the spectrum shown in Fig. 1b was obtained. This time, it was analyzed and shown to be a 48/52 mixture of **2b** and **2a**, along with (again) a small amount of the methyl radical.

The results obtained in a similar manner are summarized in Table 1.

In all cases, 313-nm light gave rise to the predominant formation of the hydrogen-abstracted radical **b** or **c**, except the amide **1** which produced a little amount of the radical; 366-nm light gave rise to the formation of a larger relative amount of the acyl radical **a** in most cases. This shows a difference in the natures of the two absorption bands in the UV spectra.⁷⁾

The hydrogen-abstracted radicals generated by 313-nm light were classified into two groups. Group-one amides (**2** and **7**) generated a radical having an unpaired electron on the carbon atom adjacent to the NH group (**b**), whereas for group-two (**1**, **3**, **5**, **6**, and **8**), the electron appeared on the carbon atom adjacent to the CO group (**c**).⁸⁾

In the case of amide **6**, a small amount of $-CH_2\dot{C}HCH_2-$ radical⁹⁾ was also observed upon irradiation with 313-nm light. Because amide **6** has an ethyl group on the carbonyl and the main hydrogen abstraction occurred on this side, the inner radical must be on the hexyl moiety on the NH group. This was confirmed by a GC–MS measurement (see below). From this experiment, the formation of three reaction products (*N*-(3-hexenyl)propanamide (**9**), *N*-hexyl-2-chloropropanamide (**10**), and *N*-(4-chlorohexyl)propanamide (**11**) was confirmed. Chloride **10** corresponds to a product from **6a**, and **9** and **11** are from the inner radical.

In some cases, the ESR spectrum after 313 or 365 nm irradiation showed the presence of alkyl radicals generated by a decarbonylation of the corresponding mother acyl radicals (**2**, **5**, and **6**).²⁾

Experimental

Amides used in this study were prepared by a condensation of the corresponding monoalkylamine and acid chloride in benzene in the presence of pyridine, and purified by several distillations under a reduced pressure. Their purities were examined by gas chromatography (column SP-1000, 100—220 °C).

ESR Measurement. A sample for ESR measurement was prepared by dissolving $FeCl_3$ (Wako Pure Chem., chemical grade) in amide ($3—5\times10^{-3}$ mol dm^{-3}) under a nitrogen atmosphere and then degassed by a freeze-pump-thaw technique (three times) in a quartz sample tube.

Photoirradiation was carried out using a USH-500D 500W ultra-high-pressure mercury lamp (Ushio Co.).

Filters for 313-nm light irradiation¹³⁾ (9% transmittance at 313 nm) were water (cell length 50 mm), aqueous potassium hydrogen phthalate (5 g dm^{-3}, cell length 10 mm), potassium chromate in 0.1% aqueous sodium hydroxide (0.2 g dm^{-3}, cell length 10 mm), aqueous nickel(II) sulfate hexahydrate (100 g dm^{-3}, cell length 50 mm), and UV-D35 glass filter (Toshiba Glass Co., 3 mm thick). Filters for 366 nm light¹³⁾ (25% transmittance at 366 nm) were water (cell length 50 mm), Pyrex glass (2.5 mm thick), UV-35 and UV-D36A glass filters (both Toshiba Glass Co., 3 mm thick).

ESR spectra were recorded by a JEOL JES-ME-3X ESR spectrometer at liquid-nitrogen temperature immediately after irradiation for an adequate period (ca. 1—20 min) at that temperature.

GC-MS Measurement of Photoirradiation Product of 6-$FeCl_3$. Amide **6** containing $FeCl_3$ was irradiated by >300-nm light for about 6 h under a nitrogen atmosphere at room temperature. The resulting mixture was extracted with hexane, followed by an examination with GC–MS (JEOL D-300 Mass Spectrometer, column PG-20E, 80—160 °C. The oven temperature was increased at a rate of 8 °C per minute). **9**: Retention time 4′35″; m/z 155 (M^+; 15), 98 ($(M-CH_3CH_2CO)^+$; 29), 70 (29), 69 ($(CH_3CH_2CH{=}CHCH_2)^+$, allylic cleavage; 100), and 57 ($CH_3CH_2CO^+$; 35). **10**: Retention time 6′25″; m/z 191 (M^+; 7), 156 ($(M-Cl)^+$; 28), 128 ($M-CH_3CHCl)^+$; 64), 123 (7), 122 (8), 121 (24), 120 (23), 85 ($(M-CH_3CHClCONH)^+$; 100), 65 (CH_3CHCl^+; 7), and 63 (CH_3CHCl^+; 20). **11**: Retention time 8′05″; m/z 193 (M^+; 3), 191 (M^+; 10), 156 ($(M-Cl)^+$; 39), 155 ($(M-HCl)^+$; 20), 114 ($(M-CH_3CH_2CHCl)^+$; 55), 100 ($(M-CH_3CH_2CHClCH_2)^+$; 25), 87 (63), 86 ($CH_3CH_2CONHCH_2^+$; 89), 74 (35), 73 ($CH_3CH_2CONH^+$; 80), 58 (64), and 57 ($CH_3CH_2CO^+$; 100).

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2) Y. Kurita, Y. Yokoyama, J. Shirokaze, and Y. Fujii, *Nippon Kagaku Kaishi*, **1982**, 1111.

3) We assigned the quintet to **2b** because **2c** is expected to give a broad triplet. The observed coupling constant of 2.1 mT is comparable to that of a radical $H_2NCONH\dot{C}HCH_3$ (A_{CH}=1.83 mT, A_{Me}=2.3 mT).⁴⁾

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6) Relative molar ratio of the radicals was determined by simulation.

7) It seems to be quite reasonable to assign the 312-nm absorption band as the CT band from Cl^- to Fe(III) and the 350-nm band as the CT band from amide to Fe(III). The former caused the generation of Cl, which might abstract hydrogen from an amide molecule. The latter generated an amide cation radical which decomposed into an acyl radical, an imine, and a proton²⁾ when irradiated on the absorption maxima.

8) We could not clarify what nature of amides would determine the course of the hydrogen abstraction. However,

there is an apparent tendency that an -X$\dot{C}$HCH$_3$ type radical (X=NH or CO) is apt to be generated.

9) g-Value=2.001, $A_H{}^{\alpha}=A_H{}^{\beta}=3.23$ mT. see; A. Lund, *J. Phys. Chem.*, **76**, 1411 (1972).

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11) Because both NH- and CO- side radicals generated from **4** would give a quintet having a similar g-value and A_H, we could not assign the observed radical. However, we think that it would be an NH-side radical, judging from the fact that the A_H value is closer to that of **2b** than to that of **3c**.

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