June, 1973] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1855—1859 (1973) 1855

The Mechanism of Photo-substitution of Ferrocene in Haloalkane-Ethanol Solutions

Takeo AKIYAMA, Akira SUGIMORI, and Horst HERMANN*
Department of Chemistry, Faculty of Science and Technology, Sophia University
Kioi-cho 7, Chiyoda-ku, Tokyo 102
**Max Planck-Institut für Kohlenforschung, Abteilung Strahlenchemie, Mülheim*
a.d. Ruhr, Bundesrepublik Deutschland

(Received January 20, 1973)

The mechanism of photo-substitution of ferrocene in haloalkane–ethanol solutions was investigated by the flash photolysis technique and other chemical methods mainly on the ferrocene–carbon tetrachloride–ethanol system. The photoreaction is initiated by the excitation of charge transfer state (electron transfer from ferrocene to carbon tetrachloride). In the absence of ethanol, CT-excitation leads to the decomposition of ferrocene to $FeCl_3$ with first order reaction kinetics of $k=(1.6\pm0.5)\times10^5\,s^{-1}$. The formation of $FeCl_3$ was inhibited by ethanol effectively to give ethyl ferrocenecarboxylate. Diethylamine quenched the formation of $FeCl_3$, whereas dimethyl sulfoxide, a stronger base than ethanol, is a less effective quencher than ethanol. These facts suggest that the most important role of ethanol is to ethanolyse trichloromethylferrocene, which otherwise decomposes to $FeCl_3$.

The solutions of ferrocene in haloalkanes are photochemically interesting systems. Brand and Snedden observed a CT-absorption ("dissociative charge transfer band") in ferrocene–haloalkane systems.[1] Körner von Gustorf and his co-workers reported that the irradiation of the system leads to the oxidation of ferrocene, to give $[Fe(C_5H_5)_2]^+[FeCl_4]^-$.[2]

Hoshi *et al.* and Akiyama *et al.* observed photochemical substitution of ferrocene in ferrocene–haloalkane–ethanol systems.[3] Ethyl ferrocenecarboxylate, ferrocenecarboxaldehyde and ethoxymethylferrocene (accompanied by di(ethoxymethyl)ferrocene) were isolated after the irradiation of ferrocene in carbon tetrachloride–ethanol, chloroform–ethanol and dichloromethane–ethanol solutions, respectively.

In order to elucidate the mechanism of photo-substitution and especially to clarify the role of ethanol, flash photolysis and several chemical methods were applied to ferrocene–carbon tetrachloride systems containing ethanol and other bases.

Experimental

Materials. For the flash photolysis study, commercial ferrocene (Rheinelbe Bergbau A.G.) was recrystallized twice from ethanol, mp 174—175 °C.

Spectro-grade carbon tetrachloride, acetonitrile and dimethyl sulfoxide, analytical-grade ethanol, dioxane and methanol and reagent-grade diethylamine (Merck A.G.) were used without further purification.

The materials used for other investigations by chemical methods were the same as described elsewhere.[3]

Flash Photolysis. The argon flash tube employed for photolysis discharged 50% of the total energy within 1.4 μs and 90% within 4.2 μs. The energy for a flash was about 10 J. The spectro-flash was similar except in energy. The spectral separation of the monitoring light was achieved by passing it through a Carl Zeiss double monochrometer equipped with a quartz prism. The light intensity was recorded photographically. The intensity of light was calibrated with standard filters. For kinetic measurements a monitoring flash lamp (G. 431 Vakuumtechnik, Erlangen) was used. The intensity of the transmitted light was followed with an oscillograph.

Solutions of ferrocene (2—5×10^{-4} mol/l) in ethanol or carbon tetrachloride containing various additives were flash photolyzed in a suprasil cell (50 mm in length and 7 mm in diameter). When necessary, the solution was deoxygenated by bubbling argon for 30 minutes.

Wavelength Dependence of Photoreaction. Monochromatic light of 436, 366, and 313 nm was obtained by passing the light from a high pressure 150 W mercury lamp (Ushio Denki Co.) through interference filters (Carl Zeiss monochromatic filter; M-436, M-365, and M-313). Light of 254 nm was obtained by passing the light from a low pressure mercury lamp (Ushio Denki Co.) through a filter solution containing potassium iodide and iodine.[4]

A deaerated ferrocene solution (279 mg ferrocene in 30 ml carbon tetrachloride–ethanol 1: 1 v/v) was irradiated in a quartz vessel by monochromatic light while being stirred continuously with a magnetic stirrer. The quantities of ethyl ferrocenecarboxylate and ferrocene were determined gas chromatographically (column; SE-30 on Diasolid L of Gaschro-kogyo Co.; temperature, 176 °C) with a Perkin-Elmer gas chromatograph Model F-6.

Actinometry was performed with a potassium trioxalatoiron(III) actinometer.[5]

Results and Discussion

Excited State Responsible for Photoreaction. The absorption spectra of ferrocene in ethanol, in carbon

---

[1] J. C. D. Brand and W. Snedden, *Trans. Faraday Soc.*, **53**, 894 (1957).

[2] E. Körner von Gustorf, H. Köller, M.-J. Jun, and G. O. Schenck, *Chem. Eng. Tech.*, **35**, 591 (1963). E. Körner von Gustorf and F.-W. Grevels, *Fortschr. Chem. Forsch.*, **13**, 365 (1969).

[3] Y. Hoshi, T. Akiyama, and A. Sugimori, *Tetrahedron Lett.*, **1970**, 1485., T. Akiyama, Y. Hoshi, S. Goto, and A. Sugimori, This Bulletin, **46**, 1851 (1973).

[4] *Cf.* In a study by UV-spectra, Traverso and Scandola reported the formation of ferrocinium ions in a ferrocene–carbon tetrachloride–ethanol system. O. Traverso and F. Scandola, *Inorg. Chim. Acta*, **4**, 493 (1970).

[4] J. G. Calvert and J. N. Pitts, "Photochemistry," John Wiley & Sons, New York, N.Y. (1966), p. 729.

[5] *ibid.*, p. 783.

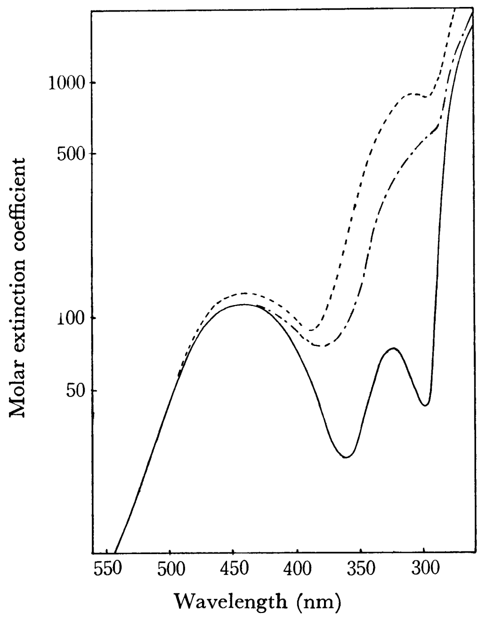


Fig. 1. UV-Spectra of ferrocene (5×10^{-3}mol/l)
—— in ethanol
--- in carbon tetrachloride
—·— in carbon tetrachloride–Ethanol (1 : 1 in volume)

tetrachloride and in carbon tetrachloride–ethanol are shown in Fig. 1.¹⁾ Scott and Becker assigned the absorption band of ferrocene at 440 nm to d-d* transition and that at 325 nm to 3d-MO*, ring MO–MO* or symmetry forbidden π-π* transition. According to them the absorption at shorter wavelength is due to π-π* or n-π* transition.⁶⁾ The absorption at 307 nm observed in carbon tetrachloride solution is due to the charge transfer excitation.¹⁾

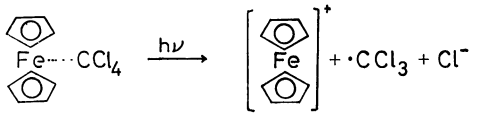
Table 1. Quantum yields in the photoreaction of ferrocene in a carbon tetrachloride–ethanol solution at various wavelengths

Wavelength (nm)	Quantum yield of ethyl ferrocenecarboxylate	Quantum yield of the decomposition of ferrocene
254	0.13	0.28
313	0.13	0.18
366	0.11	0.14
436	0.00	0.00

Wavelength dependence of the photo-substitution shown in Table 1 indicates that the excited state formed by d-d* absorption leads to no photoreaction, while the excitation of charge transfer state efficiently affords ethyl ferrocenecarboxylate. The excitation by light of a shorter wavelength brings about an increase in side reactions. Therefore, the photo-substitution arises from the electron transfer from ferrocene to carbon tetrachloride.

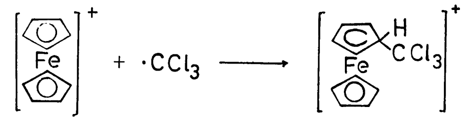
Reaction Succeeding CT-Excitation. It is known that the CT-excitation gives ferrocenium tetrachloroferrate (III) in the absence of ethanol.²⁾ However, the substitution product was obtained when ethanol is added to the above system. The problem is to clarify the role of ethanol which inhibits the decomposition of ferrocene and leads to the formation of ethyl ferrocenecarboxylate.

As reported by Brand and Snedden¹⁾ the CT-excitation yields a radical pair.



(1)

According to Beckwith and Leydon⁷⁾ ferrocenium cations are reactive toward free radicals, in contrast with ferrocene. Therefore, a reaction of the trichloromethyl radical with ferrocenium cation is plausible.



(2)

The reaction within a solvent cage would be important. The following sequence of reactions would not play an important role in this photoreaction.

(i) The formation of ferrocenium tetrachloroferrate (III), the end product in the absence of ethanol.²⁾

(ii) The reaction of ferrocenium tetrachloroferrate (III) with trichloromethyl radicals.

The reasons are:

(1) The formation of ethyl ferrocenecarboxylate is linear with respect to the light absorbed (Fig. 2), excluding a two step reaction.

(2) The UV-irradiation of ferrocenium tetrachloroferrate (III) in carbon tetrachloride–ethanol solution gave no substitution product, but ferrocene, a reduction product. In this case, we obtained a comparatively large amount of hexachloroethane, the dimerization product of trichloromethyl radicals. This indicates that ferrocenium tetrachloroferrate(III) itself has a different reactivity from normal ferrocenium ions and is unreactive toward trichloromethyl radicals.

In order to complete the substitution reaction, two reaction steps are necessary, namely;

(i) proton elimination

(ii) alcoholysis of the trichloromethyl group

The results of flash photolysis are informative. Flash

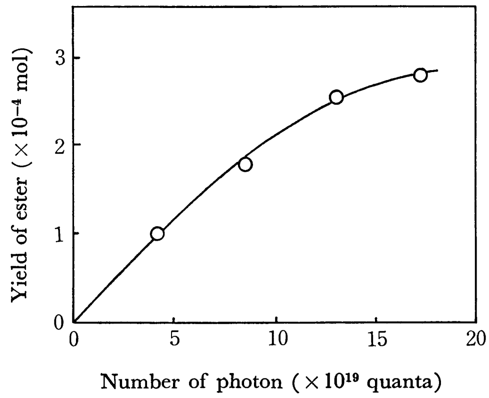


Fig. 2. The plot of the yield of ethyl ferrocenecarboxylate against quanta absorbed (at 313 nm).

---

6) D. R. Scott and R. S. Becker, *J. Chem. Phys.*, **35**, 516 (1961).

7) A. L. J. Beckwith and R. J. Leydon, *Tetrahedron Lett.*, **1963**, 385.

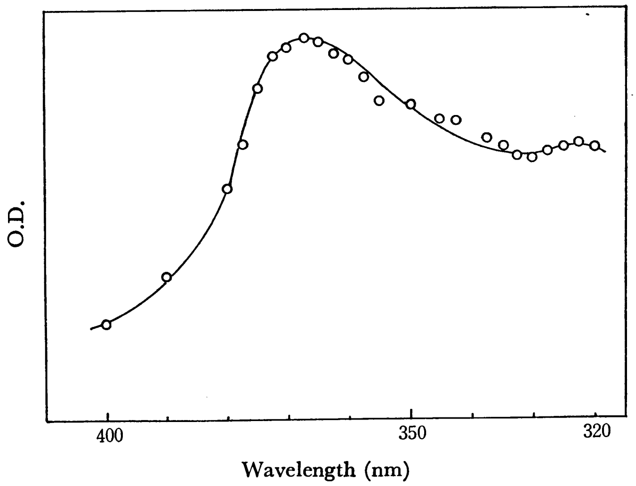


Fig. 3a. UV-Spectra of the product formed in the flash photolysis of ferrocene–CCl_4 system.

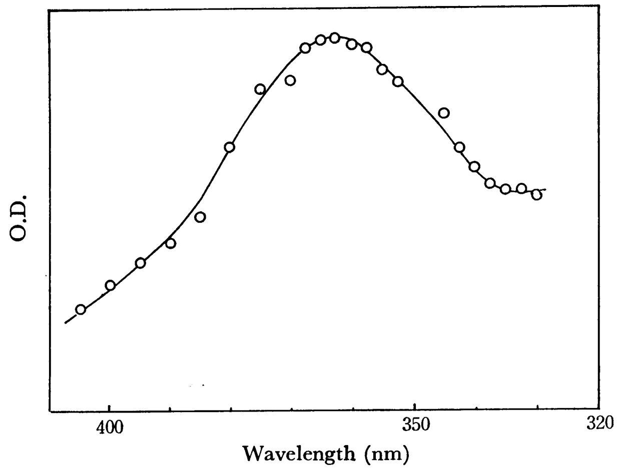


Fig. 3b. UV-Spectra of the product formed in the flash photolysis of ferrocene–CCl_4–DMSO system.

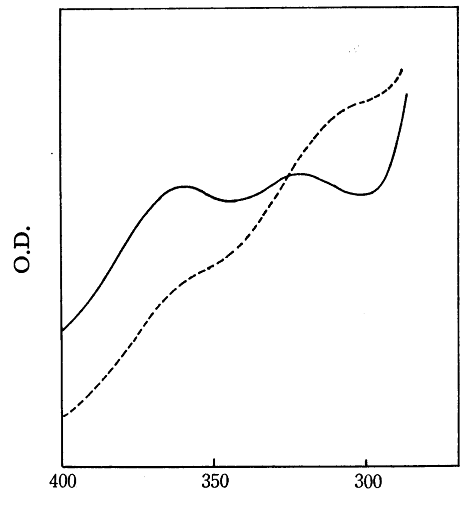


Fig. 3c. UV-Spectra of iron(III) chloride (——) and ferrocenium tetrachloroferrate (III) (– – –) in carbon tetrachloride–DMSO (DMSO 0.3 mol/l).

photolysis of ferrocene in an ethanol solution gave rise no spectral change, but that in carbon tetrachloride showed new absorption bands at 370 and 325 nm with a delay of ~μs after the photolysis flash, though no transient absorption was observed. The absorption spectra are shown in Fig. 3a. They agree with those of iron(III) chloride (λ_{max} of the UV-spectra of iron(III) chloride are 375 and 325 nm in carbon tetrachloride solution.). The spectra of the product in carbon tetrachloride containing dimethyl sulfoxide (0.3 mol/l) also agree qualitatively with those of iron(III) chloride and not with those of ferrocenium tetrachloroferrate(III), the other possible product (Figs. 3b and 3c).

The formation of iron(III) chloride was completed in about 10 μs. An example of the intensity change of the transmitted light at 370 nm through a ferrocene solution with and without photolysis flash is shown in Fig. 4.

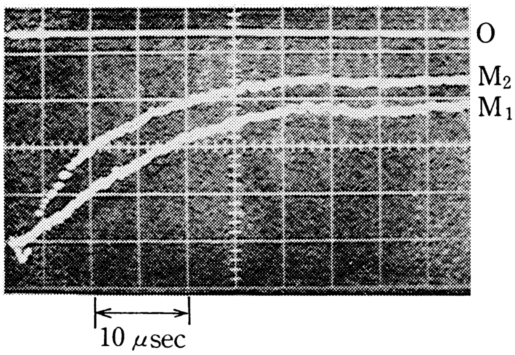


Fig. 4. The change in the intensity of the transmitted light at 370 nm.
M_1: Without photolysis flash
M_2: After photolysis flash

Kinetic analysis of the formation of iron(III) chloride is made in the following way. M_1 and M_2 are the intensities of the transmitted light without and with a photolysis flash, respectively. M_2 is smaller than M_1 due to the formation of the product. For the kinetic analysis, we should know the initial concentration of a precursor. However, the value could not be obtained in this experiment. We assume that the concentration of the precursor is equal (or proportional) to the end concentration of iron(III) chloride. Thus, we obtain the following equation for first order reaction kinetics.

$$k_1 t = \ln \frac{[FeCl_3]_\infty}{[FeCl_3]_\infty - [FeCl_3]_t}$$

where k_1 is the rate constant for a first order reaction, and $[FeCl_3]_\infty$ and $[FeCl_3]_t$ are the concentrations of iron(III) chloride after the completion of the reaction and at time t, respectively.

The expression in terms of the intensities of the transmitted light is

$$k_1 t = \ln \frac{\log (M_1/M_2)_\infty}{\log (M_1/M_2)_\infty - \log (M_1/M_2)_t}$$

In the same way, we obtain the expression for second order kinetics:

$$k_2 t = \frac{\log (M_1/M_2)_t}{\log (M_1/M_2)_\infty \{\log (M_1/M_2)_\infty - \log (M_1/M_2)_t\}}$$

TABLE 2. EFFECTS OF ADDITIVES ON THE FORMATION OF $FeCl_3$ IN THE FLASH PHOTOLYSIS OF FERROCENE–CCl_4 SYSTEM
Concentration of Ferrocene: 2×10^{-4} mol/l
Energy of one photolysis flash: ~10J
Cell: 50 mm in length

Additive	Concentration (mol/l)	Atmosphere	Increase in the extinction at 370 nm after the flash
—	—	Ar	0.32
Methanol	0.3	Ar	0.04
Dioxane	0.23	Ar	0.28
	1.2	Ar	0.30
Acetonitrile	1.9	Ar	0.16
—	—	Air	0.40
Ethanol	3.4	Air	0.33
Methanol	0.3	Air	0.42
Acetonitrile	1.9	Air	0.56
Dimethyl sulfoxide	4.2	Air	0.30
Dioxane	1.2	Air	0.61
Diethylamine	0.01	Air	0.10

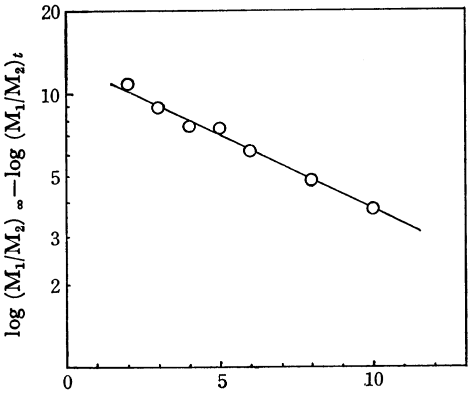
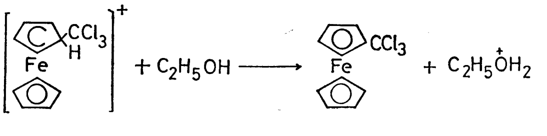


Fig. 5. First order kinetics for the formation of the product (λ_{max}=370 nm) in the flash photolysis of ferrocene–CCl_4 system.

The experimental data fit first order reaction kinetics as is thown in Fig. 5. The average first order rate constant is: $k_1=(1.6\pm0.5)\times10^5\ s^{-1}$.

The formation of iron(III) chloride was quenched by several additives. Figure 6 shows the quenching by ethanol, diethylamine and dimethyl sulfoxide in the function of the concentration of the additives. The quenching effect of ethanol is remarkable above 10^{-1} mol/l of ethanol concentration. Diethylamine is more effective and dimethyl sulfoxide less effective than ethanol. The quenching effect of other additives are summarized semi-quantitatively in Table 2.

If the most important role of ethanol in the photoethoxycarbonylation were to abstract the proton according to Eq. (3), the basicity of the proton acceptor would affect the quenching effect.



(3)

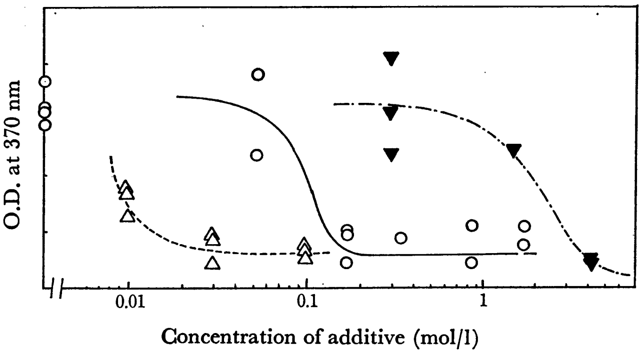


Fig. 6. Effects of additives on the formation of $FeCl_3$
△- - -△: Diethylamine, -○—○-: Ethanol,
▼- - -▼: Dimethyl sulfoxide.

Dimethyl sulfoxide is a stronger base (pK_a of the conjugate acid of dimethyl sulfoxide is 0[8]) than alcohol (pK_a of the conjugate acid of methanol is equal to −2.[8]). The quenching effect of dimethyl sulfoxide is, however, lower by one order than ethanol and methanol. This indicates that the proton abstraction step does not determine the fate of the photoreaction.

Alcohols can solvolyze trichloromethylferrocene to give a stable product, namely, the corresponding ester of ferrocenecarboxylic acid, but dimethyl sulfoxide can not perform such a reaction. The difference in quenching effect would arise from this process.

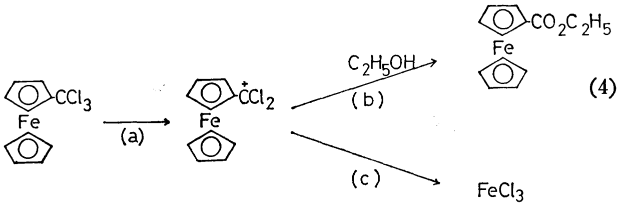
An abnormaly high rate of solvolysis was reported for α-ferrocenylethyl chloride by Hill.[9] The solvolysis is of first order with respect to the chloride. The rate constant in ethanol (40%)-ethyl ether (60%) solution at −42.8 °C and the activation energy of the reaction are $8.9\times10^{-3}\ s^{-1}$ and 10.9 kcal/mol, respectively. Hill ascribed the high rate of solvolysis to the participation of the iron atom of ferrocene.

---

[8] E. M. Arnett, "Progress of Physical Organic Chemistry," Vol. 1, ed. by S. G. Cohen, A. Streitwieser, and R. W. Taft, Interscience Publishers, New York, N. Y. (1963), p. 223.

[9] E. A. Hill, *J. Org. Chem.*, **28**, 3586 (1963).

If the solvolysis of trichloromethylferrocene is an S_N1 type reaction, the following sequence of reactions should be considered.

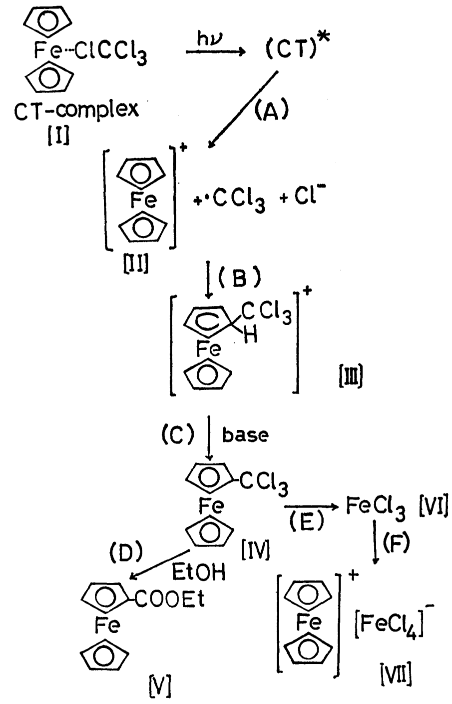


(4)

Where (a) is the rate determining process and (b) and (c) are competing processes. If this is the ca, the rate constant for process (a) should be 1.6×10^5 sec^{-1} according to our experiment. This value is large compared with that for α-ferrocenylethyl chloride (the calculated rate constant for α-ferrocenylethyl chloride at 30 °C from the data of Hill is 2.8 s^{-1}). An alternative reaction mechanism would be S_N2. We have no means of distinguishing which of these two processes actually takes place.

The presence of oxygen affects to a great extent the photochemical behavior of ferrocene, the increase in absorption at ~370 nm being greater. Alcohols hardly inhibit the increase in absorption. The shape of the spectra remained the same. This finding corresponds to the fact that the photo-substitution proceeds with no side reactions only under anaerobic conditions.

The reaction mechanism of the photo-substitution is summarized in Scheme 1.



Scheme 1.

The authors wish to thank Prof. D. Schulte-Frohlinde, Dr. G. Koltzenburg and Dr. E. Körner von Gustorf of Max Planck-Institut für Kohlenforschung for their helpful discussions. They are very grateful to Frau Ch. Kuling for her assistance in experiments. A. Sugimori thanks the Alexander von Humboldt-Stiftung for a stipend.