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Activation of Dioxygen by Radicals Formed by Charge Transfer from Ylide to TCNQ

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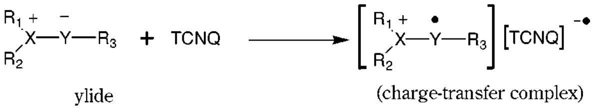
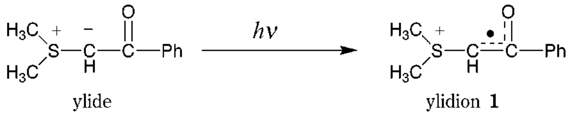
Introduction

There has been much recent interest in the activation of dioxygen, because the efficient utilization of molecular oxygen for organic synthesis is a topic of industrial importance.[4,5] We have synthesized a new type of charge-transfer complex composed of the ylide and TCNQ and have shown that this complex consists of the ylide cation radical and the TCNQ anion radical as shown:[6]



Radom et al. reported that the removal of an electron from an ylide under photoirradiation generates an odd electron cation, and this species occurs new reactions. They termed the intermediate in this reaction as "ylidion".[7] In some cases, this ylidion **1** reacts with alkenes to give additional products.[7,8] The ylide cation radical



generated by the charge-transfer complexes previously reported[6] is a species similar to the ylidion presented by Radom.[7]

The purpose of this paper is to show that the ylide cation radical and the TCNQ anion radical generated by the charge transfer from the ylide to TCNQ play an important role for the activation of molecular oxygen under photoirradiation. In this study, we used the sulfilimine as ylides. It is considered that sulfilimines, which have the polar structure of the S−N ylide bond, are suitable to the purpose of this study, because sulfilimines with higher electron density on the nitrogen atom of the S−N ylide bond function well as electron donors.

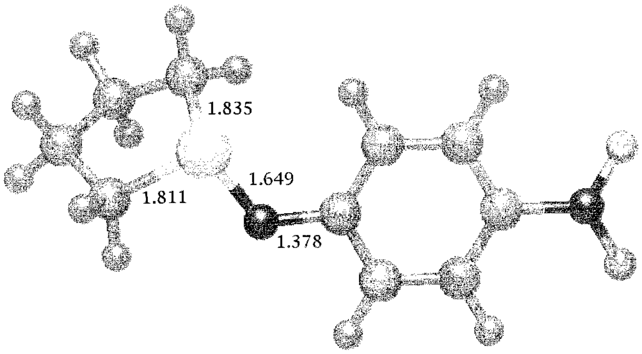


Figure 1. X-ray structure determination of *N*-arylsulfilimine **2**.[9]

We already investigated the bonding character of the S−N bond of *N*-arylsulfilimine **2** by the methods of X-ray crystal structure determination and X-ray photoelectron spectroscopy (XPS).[9] As a result, it was clarified that the S−N bond length of this sulfilimine is 1.649 Å as shown in Figure 1, and that this sulfilimine has the character of polar bonding between the sulfur and the nitrogen.

We selected sulfilimine **3** for this study. It was reported that the S−N bond length of sulfilimine **3** is 1.651 Å.[10] Thus, it is considered that the bonding character of the S−N bonds in these sulfilimines **2** and **3** is very similar and that this sulfilimine **3** is therefore one of the best candidates for this study.

We report herein the first example of the activation of dioxygen by the sulfilimine cation radical and the TCNQ anion radical.

Results and Discussion

The acetonitrile solution of sulfilimine **3** was added to the acetonitrile solution of TCNQ under air, and the pale yellow solution of the reaction mixture immediately turned to green. The experiments of photoirradiation of this reaction mixture containing the sulfilimine cation radical and the TCNQ anion radical were performed by using a low-pressure mercury arc lamp with a quartz reaction container under air. After reaction, the reaction products were obtained as a red precipitate and pure product **4** was purified by chromatography (silica gel). Spectroscopic measurements of product **4** were carried out to determine its structure.

The CO stretching band of purified product **4** was observed at 1643 cm^{-1}. The UV−visible data for product **4**, sulfilimine−TCNQ charge-transfer complex, and related compounds are summarized in Table 1. For ex-

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(1) Saitama University.

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(4) (a) Lopez, L. *Top. Curr. Chem.* **1990**, *156*, 117−166. (b) Ammon, U.; Chiorboli, C.; Dümler, W.; Grampp, G.; Scandola, F.; Kisch, H. *J. Phys. Chem.* **1997**, *101*, 6876−6882. (c)Yamada, T.; Imagawa, K.; Mukaiyama, T. *Chem. Lett.* **1992**, 2109−2111.

(5) (a) Martell, A. E.; Sawyer, D. T. *Oxygen Complexes and Oxygen Activation of Transition Metals*; Plenum Press: New York and London, 1988. (b) Yoshizawa, K.; Ohta, T.; Yamabe, T. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1911−1917. (c) Mahapatra, S.; Halfen, J. A.; Wilkinson, E. C.; Pan, G.; Wang, X.; Young, V. G., Jr.; Crammer, C. J.; Que, L., Jr.; Tolman, W. B. *J. Am. Chem. Soc.* **1996**, *118*, 11555−11574.

(6) (a) Tsuchiya, S.; Seno, M. *Chem. Phys. Lett.* **1982**, *92*, 359−361. (b) Mitomo, S.; Tsuchiya, S.; Seno, M.; Tokita, S. *Mol. Cryst. Liq. Cryst.* **1998**, *312*, 263−283.

(7) (a) Yates, B. F.; Bauma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805−5808. (b) Yates, B. F.; Bauma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1987**, *109*, 2250−2263.

(8) Zhang, J.; Schuster, G. B. *J. Am. Chem. Soc.* **1989**, *111*, 7149−7153.

(9) Tsuchiya, S.; Mitomo, S.; Seno, M.; Miyamae, H. *J. Org. Chem.* **1984**, *49*, 3556−3559.

(10) Eliel, E. L.; Koskimies, J.; McPhail, A. T.; Swern, D. *J. Org. Chem.* **1976**, *41*, 2137−2140.

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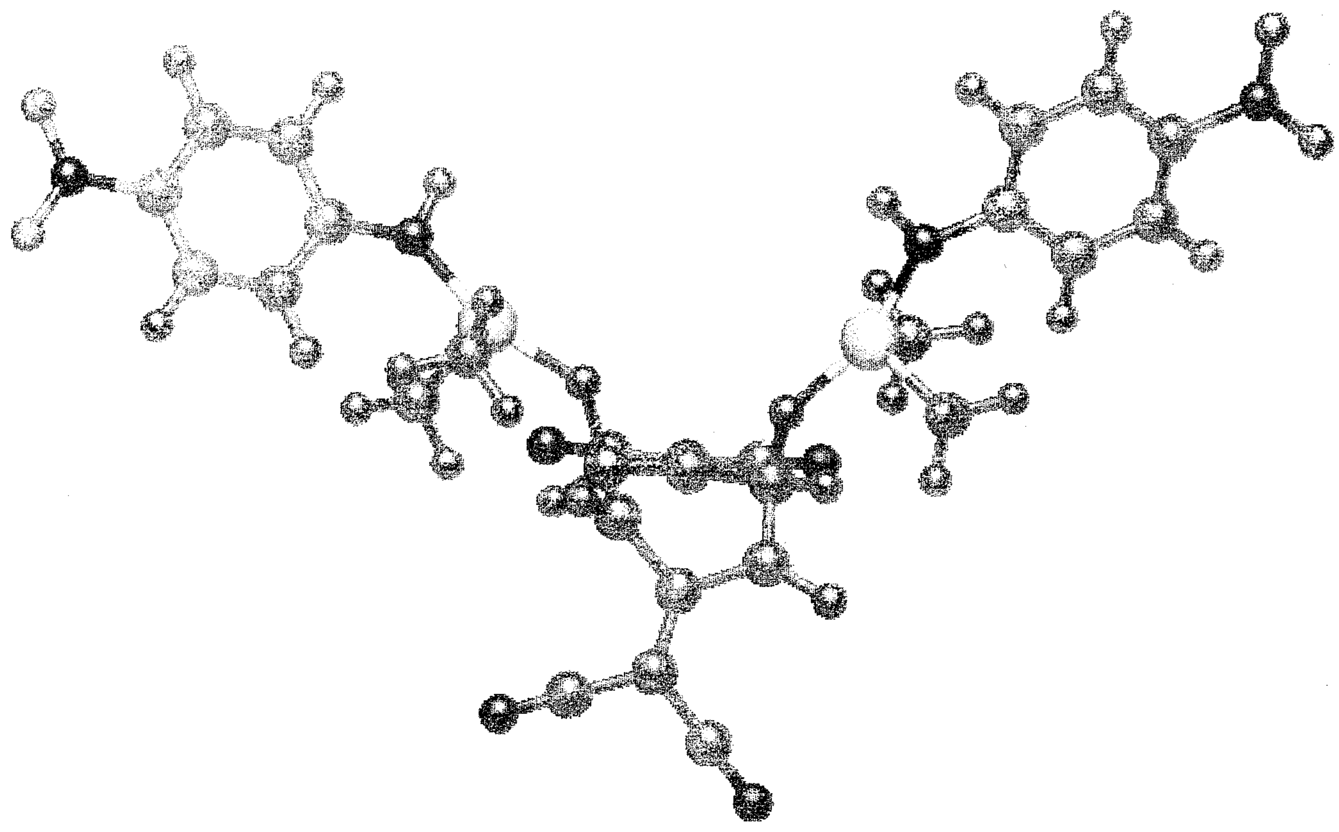


Figure 2. The conformation of product **4** optimized by the PM3 method.

Table 1. UV−Visible Data for Product 4, Sulfilimine 3−TCNQ Charge-Transfer Complex, and Related Compounds in Acetonitrile

compounds	UV−visible absorption (nm)					
sulfilimine **3**			415			
product **4**	278		480			
sulfilimine **3**−TCNQ charge-transfer complex		392		679	741	841
LiTCNQ			416	679	741	841

Table 2. NMR Data for Product 4[a]

^{1}H NMR δ (ppm)	^{13}C NMR δ (ppm)
0.9 (m, 12H, CH_3)	155.1 (*C*O)
2.3 (s, 2H, C*H*)	131.9 (C_6H_4, *C*-NO_2)
4.2 (s, 2H, N*H*)	129.6, 129.1, 123.4 (C_6H_4)
6.89−7.67 (m, 8H, C_6H_4)	115.4 (*C*-C$(CN)_2$)
	65.9 (*C*N)
	39.3 (*C*H)
	32.6, 31.3 (CH_3)

[a] Spectra were recorded in $(CD_3)_2CO$ with $SiMe_4$ as an internal reference.

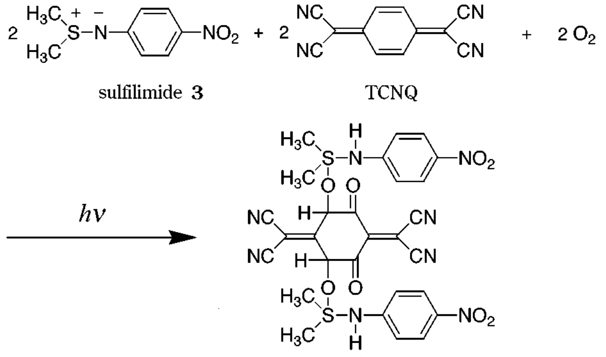
ample, the UV−visible spectra of charge-transfer complexes, which are composed of TCNQ and the sulfilimine, showed three typical peaks at 679, 741, and 841 nm due to the charge transfer. Meanwhile, the UV−visible spectrum of product **4** in the acetonitrile was different from those of the charge-transfer complexes.

The ^{1}H and ^{13}C NMR data for product **4** are summarized in Table 2. In addition, the mass spectrum for product **4** showed the parent peak at 664 (*m*/*e*), which was in agreement with the calculated value for $C_{26}H_{24}N_8O_8S_2$. The mass spectrum data of product **4** is shown in Table 3, which includes the data of related fragments to assign the structure of product **4**.

Table 3. Mass Data for Product 4

m/*e*	parent and fragments
664	parent peak product **4** (calcd mol wt 664)
648	product **4** − O atom
632	product **4** − two O atoms
168	NO_2-C_6H_4-NH-S
138	NO_2-C_6H_4-NH

The data obtained showed that product **4** is not the product of the sulfilimine and TCNQ (charge-transfer complexes) but is composed of sulfilimine, TCNQ, and O_2, indicating the structure of product **4** as shown below.



product **4**

The same reactions under argon or without light were carried out as blank experiments, but no products were obtained.[11] In addition, the TCNQ anion radical in acetonitrile did not give any reaction products under photoirradiation. The structure of product **4** shown above is also supported by the fact that total amount of the sulfilimine consumed in this reaction is more than that of TCNQ.

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[11] Experiments using O^{18} isotope were also carried out.

Under the condition without light, only sulfilimine–TCNQ charge-transfer complex was formed by the charge transfer from the sulfilimine to TCNQ. This charge-transfer complex consisted of the sulfilimine cation radical and the TCNQ anion radical as previously reported.[6,12] Several mechanisms for this reaction are considered. We had sought some evidences to clarify this mechanism. It seems to us that the important intermediates are unstable under photoirradiation. Thus, we could not isolate these compounds and did not obtain any spectroscopic data for these. Further studies on the isolation and characterization of the intermediates will be severely limited as a result of factors such as the restricted range of temperatures and solvents in which the intermediate exists as a stable species. Despite such difficulties, one plausible mechanism would be proposed by employing the present data (side product), which supplement those collected for several previously described sulfilimine–TCNQ charge-transfer complexes.[13]

An approach to evaluating the exact conformation of unusual product **4** was carried out by using PM3 and AM1 methods (WinMopac Ver 2.0), and the optimized conformation by PM3 method is shown in Figure 2.

The sulfilimine–TCNQ charge-transfer complex is a very important reagent for the activation of molecular oxygen, because the radicals that play an important role in this reaction are easily obtained by the charge-transfer reaction between the sulfilimine and TCNQ. As is stated above, it is a significant fact that the ylide cation radical and the TCNQ anion radical play an important role for the activation of dioxygen. In addition, this fact that the molecular oxygen is activated by using charge-transfer phenomenon provides new synthetic strategy.

Experimental Section

Instruments. NMR spectra of all the samples were measured by a Bruker ARX 400 spectrometer (400 MHz). Infrared spectra were recorded on a Perkin Elmer 2000 FT-IR spectrometer with KBr method. UV–visible spectra were recorded on a Shimadzu UV-2100 spectrometer. Mass spectra were recorded on a JEOL JMS-DX 303.

Reagents. TCNQ (tetracyanoquinodimethane) was obtained from KANTO Chemical Co. and was purified by several sublimations. Acetone, benzene, and chloroform were commercially available from WAKO Pure Chemical Co. and purified by distillation. Dry acetonitrile was prepared by distillation over P_2O_5 just before use. *N*-Aryl sulfilimine **3** used in this study was prepared by the published method.[14]

Reactions of the Sulfilimine with TCNQ under Photoirradiation and Oxygen Atmosphere. A solution of TCNQ (0.082 g, 0.404 mmol) in 30 mL of acetonitrile and a solution of sulfilimine **3** (0.080 g, 0.404 mmol) in 20 mL of acetonitrile were poured into a 150 mL reaction vessel. The poured solution was stirred with magnetic stirrer under air. The color of the mixture changed immediately from yellow to green. The UV–visible spectrum of this solution showed the existence of typical TCNQ anion radical (main maxima, 679, 741, and 841 nm), indicating the formation of the charge-transfer complex. After stirring for 10 min, the experiments of photoirradiation were performed with a quartz jacket at room temperature under air. A water-cooled low-pressure mercury arc lamp was used as an ultraviolet light source. The color of the solution changed slowly from green to brown under photoirradiation. In the reaction process, a product was periodically monitored by TLC. The spot increased in size until 4.5 h. Thus, the reaction time to obtain the maximum yield was determined to be 4.5 h. After reaction, the solvent of the resulting solution was removed by a rotary evaporator, and the crude products were chromatographed on a column of silica gel (C-200), with a mixture solution of acetone and benzene (1:1) as eluent. All solvents were purified by distillation. Unreacted sulfilimine and TCNQ were recovered at the same time. Then, the second purification by column chromatography was carried out by using a mixture of acetone, benzene, and chloroform (4:3:2) as eluent. The red product was obtained after evaporation of the solvent: IR (KBr) 3423 (NH), 2972, 2897, 2188 (CN), 2160 (CN), 1643 (CO), 1590, 1510, 1359, 1185, 832 cm^{-1}. Other spectroscopic data are summarized in the tables.

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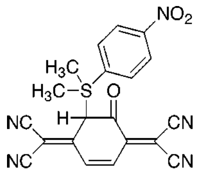
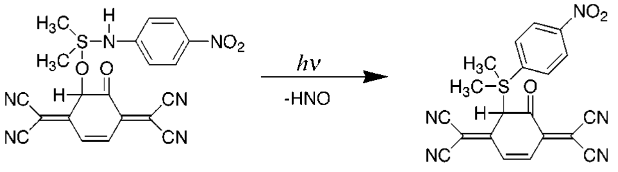
[12] The composition of sulfilimine and TCNQ in this charge-transfer complex in solution is not clear. We reported that the composition of another sulfilimine–TCNQ charge-transfer complex as a solid is 1:1.3.[6b]

[13] The isolation and the characterization of the charge-transfer complex of [sulfilimine cation radical][TCNQ anion radical] were carried out previously by us.[6,15] As is stated in the Experimental Section, the UV–visible spectrum showed the existence of the TCNQ anion radical. Additionally, this TCNQ anion radical was confirmed by ESR measurements (e.g., $g = 2.0031$, line width = 1.7 G, resonance field = 3358 G).[6,16] We tried to isolate intermediates during this reaction. However, we could not obtain any intermediates, because most of these intermediates may be very unstable under photoirradiation. However, we isolated a side product in the process of the purification of final products by column chromatography. The spectroscopic data of this side product were as follows: ^{1}H NMR δ 0.9 (m, 6H), 2.4–2.6 (m, 3H), 6.91–7.73 (m, 4H); IR (KBr) 2927, 2856, 2198, 2159, 1645, 1592, 1510, 1359, 1292, 1185, 832 cm^{-1}; MS *m/e* 402, 382, 278, 166. The structure, which was assigned by these spectroscopic data, was as follows.



side product **6**

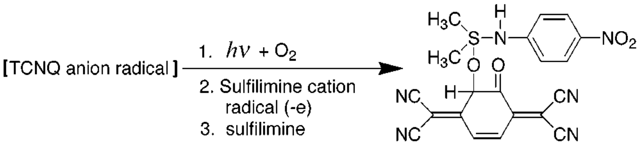
This side product would be formed by the decomposition of the intermediate under photoirradiation as shown.



intermediate **5** side product **6**

Thus, one plausible mechanism proposed by us is as follows.

Sulfilimune **3** + TCNQ → [Sulfilimine cation radical] [TCNQ anion radical]



intermediate **5**

$$\text{intermediate } \mathbf{5} \xrightarrow[\text{3. Sulfilimine cation radical (-e)}]{\text{1. sulfilimine} \quad \text{2. } h\nu + O_2} \text{Product } \mathbf{4}$$

[14] Claus, P. K.; Rieder, W.; Hofbauer, P. *Tetrahedron* **1975**, *31*, 505–510.

[15] Tsuchiya, S.; Mitimo, S.; Kise, H.; Seno, M. *J. Chem. Soc., Perkin Trans. 2* **1986**, 245–247.

[16] Tsuchiya, S.; Mitimo, S.; Seno, M. *J. Chem. Soc., Chem. Commun.* **1983**, 340–341.