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Chemiluminescence from Reactions of $N_2^*(A^3\Sigma_u^+)$ with Solid Organic Compounds at 77 K

Kenichi Mitsumori and Kenzo Hiraoka*
Faculty of Engineering, Yamanashi University, Takeda-4, Kofu 400

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The luminescence from reactions of $N_2(A^3\Sigma_u^+)$ with solid benzene, toluene, hexane, cyclohexane and those doped with biacetyl at 77 K has been investigated. For benzene, a broad band appeared in the range of 350—550 nm whose radiative lifetime was determined to be 2.5 s. This band was largely eliminated by addition of a small amount of biacetyl, indicating the participation of an intermediate excited state in solid benzene, *i.e.* triplet excitons. The emitter of the broad band was tentatively assigned to reaction products, possibly benzene isomers. For toluene, a strong appearance of benzyl radical emission was observed. With an addition of biacetyl, the elimination of benzyl emission and a strong growth of biacetyl phosphorescence were observed as for the benzene/biacetyl system. With an increase of biacetyl concentration, a remarkable red shift were observed for biacetyl phosphorescence, while no shift was observed for benzyl emission, indicating the difference of the solvent effect for these electronic transitions. No luminescence was observed for solid hexane and cyclohexane.

The major difficulty in elucidating the reaction mechanisms of reactions of active nitrogen with organic compounds was mainly due to the existence of several active species in active nitrogen which were produced by electrical discharge. The major active species in active nitrogen are long-lived $N(^4S)$ and $N_2(A^3\Sigma_u^+)$.[1] The rate constants for the reactions of $N(^4S)$ with organic compounds have been measured,[2,3] but the reported data are not in good agreement with each other, possibly owing to the contamination of $N(^4S)$ with $N_2(A)$. In order to elucidate the reaction mechanisms of active nitrogen unequivocally, it is indispensable to isolate the active species and study its reactions with organic compounds.

So far only a few investigations have been performed which dealt with $N_2(A)$.[4–6] Dessaux[4,5] reported a simple method for producing "pure" $N_2(A)$ by passing active nitrogen (discharged N_2) through a liquid nitrogen cooled trap. By this method, $N_2(A)$ in the absence of N atoms can be made available owing to the favorable recombination of nitrogen atoms on the cold surface of the trap. Devolder[6] observed the disappearance of ESR signals of nitrogen atoms after passing the active nitrogen through the cold trap at 77 K. Dessaux[4] observed the phosphorescence from the reaction of $N_2(A)$ with solid benzene and he concluded that the emitter of the phosphorescence is the charge transfer complex of $N_2(A)$ and C_6H_6, *i.e.* $N_2(A)^{\pm}\cdots C_6H_6^{\mp}$. We think that Dessaux's conclusion is less likely because the phosphorescence spectrum is very similar to those observed for solid benzene induced by electron impact.[7,8] In this work, the emission spectra from the reactions of $N_2(A)$ with various solid oragnic compounds were measured in order to obtain information on the reaction of $N_2(A)$ with organic compounds at 77 K.

Experimental

The nitrogen gas (0.5 Torr†, Nippon Sanso ultra pure, 99.99999%) was passed through a trap at 77 K and led to a microwave cavity. The active nitrogen generated was passed through a second trap at 77 K and then flowed to the cold finger at 77 K on which organic compounds were deposited. The vacuum system was made of greese-free Pyrex glass. In the presence of nitrogen atoms, a characteristic yellow afterglow (first positive band, $B^3\Pi_g \rightarrow A^3\Sigma_u^+$) was observed which is due to the reaction $2N+M=N_2^*+M$. The yellow afterglow disappeared completely on passing the active nitrogen through the trap at 77 K. The flow speed of N_2 was 4 m/s.

For luminescence measurements, a quartz window was placed on the port of the vacuum system opposite the side face of the cold finger. An Optech GM-N-250 monochromator with a Hamamatsu TV-R585 photomultiplier was positioned in front of the window. A synchronous motor was used to scan the grating and the output from the monochromator was detected by a Hamamatsu TV-C1230 photon counter, and displayed on an x-y recorder. The resolution of the monochromator was 7 nm.

All samples except benzene were Tokyo-Kasei extra pure. Benzene for fluorometry was purchased from Merck. Samples were vacuum degassed prior to inletting by multiple freeze-pump-thaw cycles.

Results and Discussion

Benzene. In Fig. 1(a) is shown the emission spectrum from a reaction of $N_2(A)$ with solid benzene at 77 K. A broad band with a maximum at 400 nm (hereafter, cited as band A) was observed. The decay of the luminescence was recorded by setting the monochromator at the maximum wavelength, following the manual shutting off of the excitation power over a period of time. The lifetime of the luminescence was determined to be 2.5 s, in good agreement with the value obtained by Dessaux.[4] Dessaux suggested that the emitter of the long-lived phosphorescence is the charge transfer complex of $N_2(A)$ with C_6H_6, *i.e.* $N_2(A)^{\pm}\cdots C_6H_6^{\mp}$. If the charge transfer complex $N_2(A)^{\pm}\cdots C_6H_6^{\mp}$ was really formed on the surface of solid benzene, the quenching of this state by the energy transfer to the impurity molecules should be inefficient because of the localization of the charge transfer complex in the benzene matrix. In order to investigate the energy transfer processes in solid benzene, the luminescence spectra of solid benzene doped with biacetyl were measured as a function of the concentration of biacetyl. As shown in Fig. 1, by doping biacetyl in solid benzene,

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† 1 Torr = 133.322 Pa.

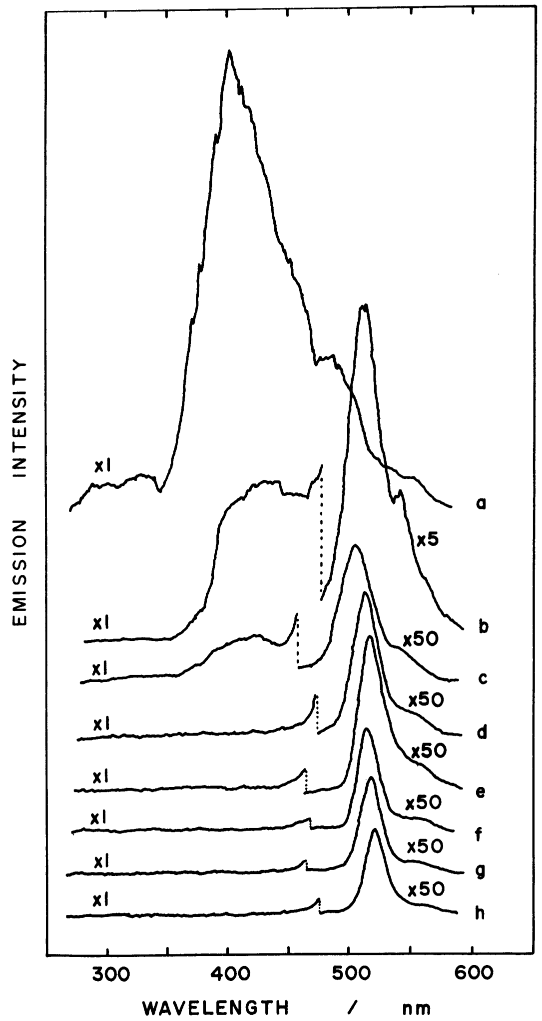

Fig. 1. The luminescence spectra from the reaction of $N_2(A^3\Sigma_u^+)$ with solid benzene doped with biacetyl at 77 K. The mol% of biacetyl in biacetyl–benzene solid solution are: (a) 0, (b) 0.1, (c) 1.0, (d) 5.1, (e) 10.2, (f) 20.4, (g) 50.6, (h) 100.

a remarkable suppression of the band A and an appearance of a characteristic phosphorescence of biacetyl are observed. This result indicates the importance of energy migration in the benzene matrix after the triplet electronic energy transfer from N_2(A) to the benzene molecule. Apparently, the emission of the band A is induced by the long-range energy transfer of triplet excitation in solid benzene. The possibility that the emitter of the band A is the charge transfer complex is, therefore, unlikely. The experimental results described above led us to conclude that the luminescence from the reaction of N_2(A) with solid benzene is due to the emission of some reaction products produced in the benzene matrix.

It is worthwhile noting that the emission spectrum shown in Fig. 1(a) is very similar to that observed for solid benzene induced by electron impact.[9,10] When an ultrathin film of benzene deposited under vacuum at 77 K was bombarded by low-energy electrons ($<\approx$10 eV), only a benzene fluorescence ($^1B_{2u} \rightarrow {}^1A_{1g}$) was observed.[9] With the increase of the incident electron energy ($\geq\approx$20 eV), new bands with maxima at 295 and 400 nm appeared. These bands could still be observed when the incident electron energy was decreased below 10 eV. This result strongly suggests that the emitters of these bands are the radiation products formed in the solid benzene film.

Phillips and Schug[10] also observed the broad band appearing at 400 nm under the stimulation of solid benzene by 1 MeV electrons. They assigned this band to the triplet and triplet excimer emission. We think that their assignment is dubious because the observation of emission from the triplet state in pure organic crystals has been unsuccessful due to the triplet excitation migration and the rapid triplet-triplet annihilation. The large exchange resonance interaction is no doubt a general phenomenon for π-electron system and it corresponds to a transition time for excitation transfer between nearest neighbors of less than 10^{-12} s.[11]

As described previously, the luminescence of benzene induced by electron impact consists of 295 and 400 nm bands as well as the benzene monomer fluorescence at 270 nm. In Fig. 1, a weak band at 290 nm is observed as well as the strong band A at 400 nm. The emitters of these bands seem to be the same for both of these experiments. Quite a few studies have been made of the vacuum-ultraviolet photochemistry of benzene.[12] Benzene irradiated by ultraviolet radiation in the gas and liquid phase is known to undergo isomerization to yield benzene isomers, *i.e.*, mainly benzvalene and fulvene.[13] Although no luminescence of these benzene isomers has been reported, we would like to propose that the 290 nm band and the 400 nm band are fluorescence and phosphorescence of a benzene isomer produced in the benzene matrix. The weak fluorescence of the benzene isomer at 290 nm would be induced by the energy transfer from the singlet excitons which are formed by the homofusion of triplet excitons in the benzene matrix. The formation of benzene isomers from triplet states' benzene has not been reported before,[††] but the temperature-dependent radiationless transitions from T_1 are attributed to transitions to an isomeric singlet state.[14] The identification of the benzene isomer could not be done at the present stage. The emitter of the 325 nm band in Fig. 1 could not be specified either. A more detailed investigation is apparently needed in these respects.

With decreasing concentration of biacetyl from 100 to 10 mol%, the phosphorescence intensity of biacetyl shows a gradual increase. This suggests that the efficiency of the energy transfer from N_2(A) to biacetyl is smaller than that from triplet benzene to biacetyl. This seems reasonable because the energy difference between triplet states of N_2(A) and biacetyl is appreciably larger than that between benzene and biacetyl and the energy transfer efficiency for the former pair is considered to be smaller than that for the latter pair (Dexter's theory[15]).

With increase of the concentration of biacetyl, the phosphorescence spectrum of biacetyl shows a red shift as shown in Fig. 1. This indicates that the degree

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[††] Energetically, $N_2(A^3\Sigma_u^+)$ could excite benzene molecules up to T_3.

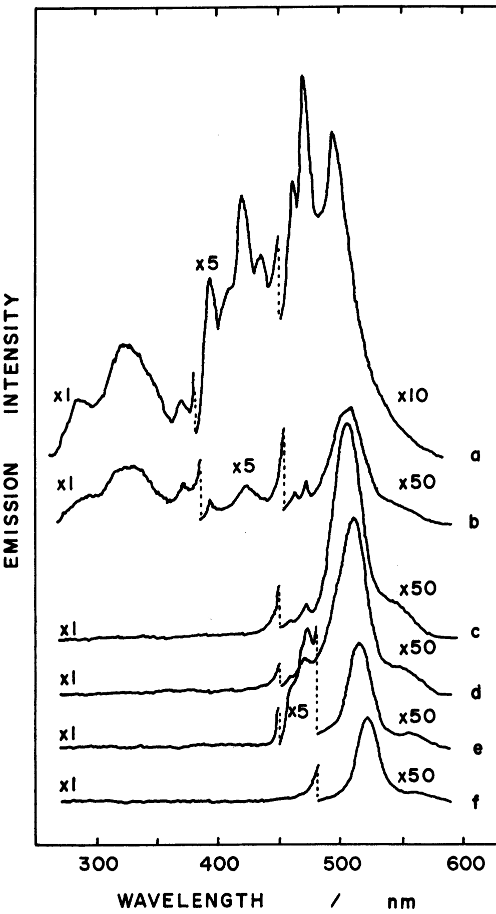

Fig. 2. The luminescence spectra from the reaction of $N_2(A^3\Sigma_u^+)$ with solid toluene doped with biacetyl at 77 K. The mol% of biacetyl in biacetyl-toluene solution are: (a) 0, (b) 0.1, (c) 5.9, (d) 23.0, (e) 54.4, (f) 100.

of solvation of triplet biacetyl by benzene molecules is different from that by biacetyl molecules. Because the polarizability of benzene (10.3 Å^3) is larger than that of biacetyl (9.2 Å^3), the larger solvation energy of biacetyl would be due to its intramolecularly dipolar property. The observation of the red shift of biacetyl phosphorescence indicates that a considerable degree of solvation of the triplet state of biacetyl (*i.e.* rotation of solvent molecules) takes place in rigid solid at 77 K during the lifetime of this state ($\approx 2.25\times10^{-3}$ s[16]).

After the measurements of luminescence, the benzene sample was analysed by gas chromatography. No gaseous or liquid products were deteced. The formation of solid products was not observed either on the wall of the cold finger after the evaporation of the benzene sample.

Toluene. The luminescence spectrum from reactions of $N_2(A)$ with solid toluene at 77 K is shown in Fig. 2(a). The three longest-wavelength lines beginning at about 460 nm are easily identified as the fluorescence of the benzyl radical.[17] By doping with 0.1 mol% of biacetyl, a strong emission of biacetyl phosphorescence appeared, clearly indicating the migration of triplet energy in solid toluene. The benzyl emission showed a rather gradual suppression when the biacetyl concentration was increased. In contrast to the case of benzene/biacetyl system the benzyl emission was still observed with a biacetyl concentration of 54 mol%. Because the emission of the benzyl radical by a single collision of $N_2(A)$ with toluene is endoergic, the persistence of benzyl emission must be due to the high concentration of benzyl radicals formed in the toluene matrix.

In addition to the benzyl emission, sharp emission lines are observed in the range of 380—440 nm (Fig. 2(a)). Phillips and Schug[10] also observed similar emission lines from solid toluene induced by 1 MeV electrons. They proposed the benzyl ion to be the most probable candidate for this emission. Although the ionization energy of benzyl radical (7.27 eV[18]) is about 1 eV higher than the available energy of $N_2(A)$ (6.17 and 6.30 eV for $v'=0$ and $v'=1$, respectively), the ionization of benzyl radicals in the solid toluene by $N_2(A)$ could be energetically possible because the polarization energies of ions in solid organic compounds are generally higher than 1 eV.[19–21] For $N_2(A)$, the favored Franck-Condon factors tend to reduce the available energy from 6.17 eV to $\approx$4.7 eV, and this might explain the relatively weak emission of these lines compared to the results obtained by Phillips and Schug.[10] Almost a complete elimination of these emission lines is observed with the addition of 5 mol% of biacetyl, indicating that the concentration of the emitter of these bands is much lower than that of benzyl radical.

Two short-wavelength lines appearing weakly at 290 and 325 nm are observed. These bands could be assigned to monomer and excimer fluorescences of these compounds. The excited singlet states can be formed by a homofusion of triplet excitons (triplet-triplet annihilation) in the solid matrix. The assignment of the band at 325 nm as an excimer emission may not be conclusive because solid thin films of benzene and toluene bombarded by electrons gave only the monomer fluorescence and the excimer emission was not observed.[9,22] These results indicate that solid benzene and toluene deposited at 77 K were crystalline. Thus the band at 325 nm may not be due to the excimer but to some other reaction products.

As in the benzene/biacetyl system, phosphorescence spectra of biacetyl show a red shift with an increase of the concentration of biacetyl as shown in Fig. 2. On the contrary, the emission spectra of the benzyl radical appearing at 465 and 475 nm do not show any noticeable shift with an increase of biacetyl concentration. This indicates that the ground and excited benzyl radical are almost equally solvated by solvent toluene or biacetyl. This seems reasonable because the distributions of a nonbonding electron for the ground and excited states of benzyl radical are highly delocalized owing to the π-electron character of the nonbonding electron.

Alkanes. No chemiluminescence was observed for the reactions of $N_2(A)$ with solid hexane or cyclohexane at 77 K. With an addition of 0.1 mol% of biacetyl in solid hexane or cyclohexane, only a very weak phosphorescence of biacetyl was observed. Its intensity was about 0.1% of the phosphorescence of solid benzene doped with the same amount of biacetyl. The weakness of the phosphorescence suggests that the phosphorescence was induced by the direct energy transfer from $N_2(A)$ to biacetyl. Apparently an efficient triplet energy migration does not occur in solid alkanes. The absence of the energy migration suggests either that the energy transfer from $N_2(A)$ to alkanes does not occur or that the triplet energy transfered to alkanes does not migrate in the solid matrix. From the results obtained by the ultraviolet absorption spectroscopy and the low-energy electron impact spectroscopy,[23] it is known that a characteristic feature of alkanes is the absence of observable excitation below about 7 eV. This lower limit of energy for the excitation is about 1 eV higher than the available energy of $N_2(A)$ and the energy transfer from $N_2(A)$ to alkanes is endoergic. Actually neither gaseous nor solid products were detected by GC or FT-IR after the reaction of $N_2(A)$ with solid alkanes at 77 K for more than 10 h.

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