

ELECTRON SPIN RESONANCE AND OPTICAL SPECTROSCOPIC INVESTIGATIONS OF THE REACTIONS OF ACTIVE NITROGEN WITH A FEW HOST-GUEST MIXED POLYCRYSTALS AT 77 K

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Summary

Chemiluminescences are emitted by the cold hydrocarbon surface during the reaction of active nitrogen with (host) polycrystals or glasses doped with an aromatic guest and condensed on a cold finger at 77 K. These active-nitrogen-induced chemiluminescences exhibit the following features: (i) with a polycrystalline host (aromatic or not) the guest phosphorescence is emitted; (ii) no chemiluminescence is observed with a glassy host; (iii) with a methyl-substituted benzene derivative, as a host or as a guest, the derived benzyl-like radical fluorescence is emitted. Both emissions (guest phosphorescence and radical fluorescence) are proportional to the square of the nitrogen atom $N(^4S)$ concentration. Weak deferred luminescences are emitted by the hydrocarbon polycrystal after the reaction of active nitrogen. The main feature of the electron spin resonance spectra is the presence of cyclohexadienyl-type radicals. All these spectroscopic results (chemiluminescences and deferred luminescences) can be accounted for by the following mechanism: (i) two-body recombination of nitrogen atoms on the cold hydrocarbon surface and (ii) energy transfer from the $^3\Sigma_u^+$ state of nitrogen to either the guest triplet state or the radical excited doublet state. A parallel is suggested with the well-known characteristics of two-quanta reactions.

1. Introduction

The reaction of active nitrogen with cooled hydrocarbon surfaces has been the subject of a few spectroscopic studies [1 - 5]. Faure and coworkers [1] have recorded the phosphorescence emitted during or after condensation at about 4 - 20 K of a flow of active nitrogen containing various aromatic additives. By reaction of "cooled" active nitrogen* with a variety of pure

*In "cooled" active nitrogen, the active nitrogen is flowed through a trap at 77 K; using this procedure the nitrogen atom concentration is reduced by a factor of about 20.

aromatic hydrocarbons Dessaux and Demary [2] have observed luminescences assigned to charge transfer phosphorescences; they have also observed naphthalene phosphorescence with naphthalene-doped benzene and benzyl radical fluorescence with toluene. Electron spin resonance (ESR) spectroscopy has been used by Forchioni and Chachaty [3] and by Minkwitz and Froben [4]; Froben has also recently reported spectroscopy measurements.

In this paper we are concerned with the chemiluminescences emitted by the reaction of active nitrogen with solid hydrocarbon surfaces cooled to 77 K. We shall deal with the various aspects of this chemiluminescent reaction.

(1) The identification of the chemiluminescence emitter is achieved using optical emission spectroscopy.

(2) The paramagnetic species within the flow of active nitrogen and the free radicals formed in the hydrocarbon polycrystal during the reaction are monitored by ESR spectroscopy. The relation between the chemiluminescence intensity and the nitrogen atom concentration is also investigated.

(3) When the flow of active nitrogen is stopped, the chemiluminescence intensity exhibits a rapid decrease (within a few seconds) to a stationary very low (but different from zero) level. This faint "deferred" luminescence may usually be seen with the naked eye up to 30 min after the flow of active nitrogen has been stopped. A qualitative limited spectroscopic investigation of this deferred luminescence is carried out for the naphthalene-benzene mixed polycrystal.

2. Experimental section

2.1. Apparatus and chemicals

Nitrogen (quality U from l'Air liquide, 99.99%) is flowed through one trap at 77 K before entering the microwave (2450 MHz) cavity. Active nitrogen is then flowed to the cold finger at 77 K (diameter, 6 mm for ESR and 5 cm for optical spectroscopy). The hydrocarbon mixture, previously degassed, is condensed onto the cold finger before or simultaneously with the flow of active nitrogen. The vacuum line is completed by a trap, a Pirani gauge and a pump. The whole apparatus prior to the cold finger is made of Pyrex, is grease free and contains a short extension which acts as a light trap to avoid a possible photoionization by the UV light from the microwave discharge.

The hydrocarbons are of spectroscopic grade or of the highest purity available commercially. The deuterated compounds benzene-d₆ (99.6%) and naphthalene-d₈ (98.6%) were purchased from Service des Molécules marquées du Commissariat à l'Energie Atomique.

A test experiment with ultrapure nitrogen (N48, 99.998%, from l'Air liquide) and gas-chromatographed benzene solvent gave the same experimental results.

ESR spectra are recorded with either a Varian V 4502 or a Varian E 109 spectrometer. For optical spectroscopy the chemiluminescence light, which

reaches its maximum intensity in front of the incoming nitrogen flow, is analysed with a Coderg scanning monochromator (0.3 m, Czerny–Turner) and an EMI 9558 QA (S20) photomultiplier (uncorrected for spectral response) and is then displayed on a Servotrace PES 25 chart recorder.

2.2. Operating conditions

Before every experiment the vacuum line is “washed” by flowing active nitrogen for about 30 min. After condensation of the hydrocarbon vapour, the yellow nitrogen afterglow film around the cold finger is not restored but is replaced by the chemiluminescent hydrocarbon surface. For the nitrogen pressures of below 5 Torr used at present, the nitrogen afterglow emitted by the active nitrogen gaseous flow is undetectable when the apparatus sensitivity is set for optimum recording of a chemiluminescence spectrum.

3. Experimental results

3.1. Optical spectroscopy

3.1.1. Chemiluminescence spectra

Active nitrogen is allowed to react with the doped or pure polycrystals or glasses listed in Table 1. The host (or solvent) is in general a benzene polycrystal. The guest (or solute) concentration is typically 10^{-2} - 10^{-1} M. The particular spectrum observed for the reaction of active nitrogen with pure benzene has been analysed elsewhere [6].

The same chemiluminescence spectrum is always observed whether the hydrocarbon host–guest mixture is allowed to react in the gas phase within the flow of active nitrogen prior to condensation on the cold finger or whether

TABLE 1

Chemiluminescences observed during the reaction of active nitrogen with mixed host–guest polycrystals

Guest	Host					
	Benzene- h_6 or benzene- d_6	Pyridine	Cyclohexane	Ethanol	Methyl- cyclohexane	Toluene
Naphthalene- h_8 or naphthalene- d_8	P, DL	P	P, DL			P, f
Carbazole	P					
Benzophenone	P, DL					
Acetophenone	P, DL			O		
Benzaldehyde	P					
Benzonitrile	P, DL	P		O	O	P, f

P, emission of the guest phosphorescence during the reaction; f, emission of the benzyl radical fluorescence during the reaction; DL, emission of a deferred luminescence after the reaction; O, no chemiluminescence is emitted.

a luminescence the intensity of which is roughly a function of the nitrogen pressure. Under these conditions the effect of the room temperature gas flow is sufficient to increase the temperature of the hydrocarbon surface and thus to induce the thermoluminescence emission. For gas pressures above 10 Torr the whole thermoluminescence, typically emitted within a few minutes, exhibits a broad spectrum in rough accord with the chemiluminescence spectrum. These observations are not unexpected since it is well known that, after radiolysis of aromatic solutes in glassy matrices, the main feature of the observed thermoluminescences is the solute phosphorescence [8 - 11] (or the benzyl radical fluorescence with toluene as a solute [11]).

To summarize, the reaction of active nitrogen is followed by two distinct deferred luminescences: an isothermal luminescence and a thermoluminescence. A few experimental observations suggest that the deferred luminescence spectrum is identical with the chemiluminescence spectrum. Furthermore, the deferred luminescences following the reaction with active nitrogen exhibit strong similarities to the deferred luminescences following radiolysis or photoionization [8 - 11].

3.2. Electron spin resonance spectroscopy

ESR spectroscopy is used to identify the radicals formed during the reaction of active nitrogen with the cooled hydrocarbon surface. Whereas every chemiluminescence spectrum is found to be characteristic of the guest, the reverse holds for the radicals observed after the reaction of active nitrogen with aromatic hydrocarbons. The ESR spectrum is associated with the main component of the hydrocarbon mixture, *i.e.* the host; for instance, the same ESR spectrum is observed after reaction of active nitrogen with benzene either in the pure state or containing guests such as naphthalene, carbazole, toluene or *p*-xylene.

The ESR spectra are often badly resolved but a common feature is the presence of cyclohexadienyl-type radicals after the reaction with benzene or its substituted derivatives.

3.2.1. Reaction of active nitrogen with benzene polycrystals

A typical ESR spectrum recorded after the reaction of active nitrogen with benzene either in the pure state or containing a solute is presented in Fig. 1. The two lateral quadruplets are readily assigned to the cyclohexadienyl radical $C_6H_7^{\cdot}$ [13].

A comparison of the experimental spectrum (Fig. 1(a)) with a simulated ESR spectrum of $C_6H_7^{\cdot}$ (Fig. 1(d)) shows undoubtedly that another radical is present in the central part of the spectrum of Fig. 1(a). This radical, which exhibits a much smaller spectral width than does $C_6H_7^{\cdot}$, is tentatively assigned to the phenyl radical $C_6H_5^{\cdot}$ on the following basis.

(1) The phenyl radical is stable in a benzene matrix up to about 130 K [14, 15].

(2) A stick diagram of $C_6H_5^{\cdot}$ with hyperfine splitting constants taken from ref. 15 is in rough agreement with our spectrum. A true simulation sim-

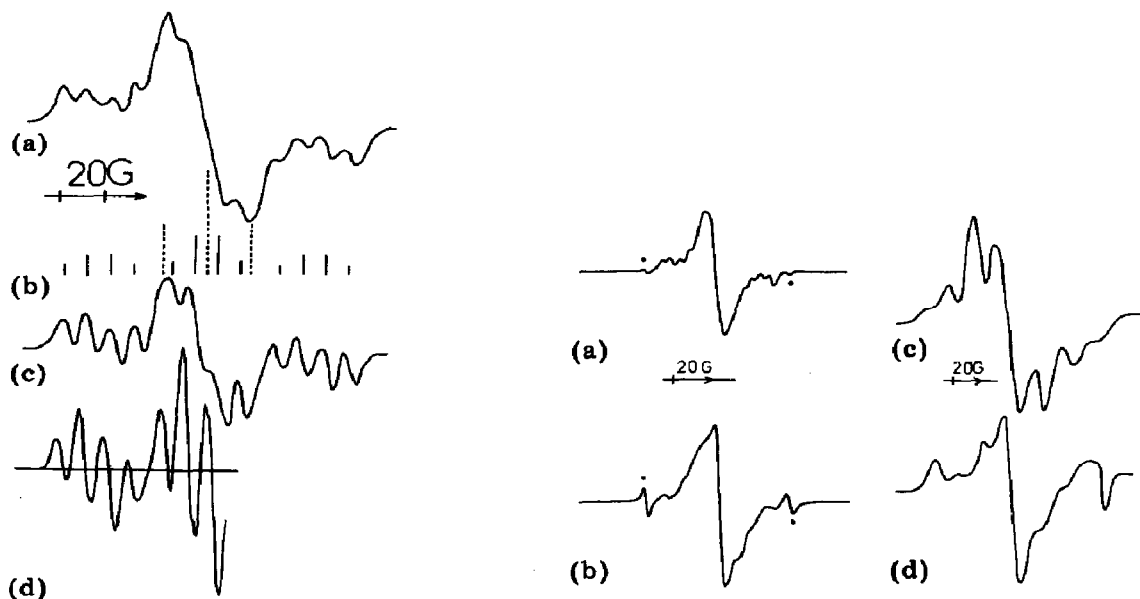


Fig. 1. ESR spectra observed after the reaction of active nitrogen with a benzene polycrystal at (a) 77 K and (c) 150 K. (b) A stick diagram of the ESR spectra of the cyclohexadienyl radical (—) and the phenyl radical (- - -) in equal concentrations. (d) A simulated ESR spectrum of the cyclohexadienyl radical.

Fig. 2. ESR spectra observed after the reaction of active nitrogen with (a) a benzene-toluene polycrystal, (b) *p*-xylene, (c) *p*-chlorotoluene and (d) biphenyl. ●, these peaks belong to the (weak) ESR spectrum of the $\text{CH}_2\text{N}^\cdot$ radical.

ilar to that for $\text{C}_6\text{H}_7^\cdot$ is difficult for $\text{C}_6\text{H}_5^\cdot$ because of the large anisotropy of g and the hyperfine tensors and the high sensitivity of these tensors to the nature of the matrix [14, 15].

(3) Our observed ESR spectrum is quite similar to the spectra recorded after γ radiolysis of benzene which have been assigned to the simultaneous presence of $\text{C}_6\text{H}_7^\cdot$ and $\text{C}_6\text{H}_5^\cdot$ [13].

(4) It has been shown with ESR spectroscopy [3, 16] that the usual radical observed after the reaction of active nitrogen with a variety of hydrocarbons results from the elimination of the less-bonded hydrogen atom. Likewise our present optical spectroscopic study clearly shows that benzyl-type radicals are routinely formed; thus the formation of phenyl radicals in a benzene polycrystal is not unexpected.

These experimental and bibliographic arguments support our tentative assignment of the observed spectrum to the simultaneous presence of $\text{C}_6\text{H}_7^\cdot$ and $\text{C}_6\text{H}_5^\cdot$ radicals. Nevertheless, a question arises from the present observation of deferred luminescences. It is well known that the deferred luminescences following radiolysis are caused by the recombination of charged species [8, 9]. Thus, the presence of charged species (electrons, anions, cations) could also account for the central part of the observed spectrum, but under our experimental conditions the contribution of such charged species is apparently very low for the following reasons: (i) we have observed (Section 3.1.2)

that the irradiation of the hydrocarbon surface with visible light leads to the disappearance of any deferred luminescence whereas the ESR spectrum is unchanged; (ii) the probability for an electron to be trapped is much lower in a polycrystal than in a glass [8].

3.2.2. Reaction of active nitrogen with other aromatic hydrocarbons (Fig. 2)

As outlined earlier, a common feature of all the observed ESR spectra is a large total spectral width of about 130 G, similar to that in benzene. By analogy with benzene, this large spectral width may be assigned to the presence of cyclohexadienyl-type radicals since, for all the substituted cyclohexadienyl radicals studied [13, 17 - 19], the two out-of-plane CH_2 protons have hyperfine splittings of about 40 - 50 G whereas those of the in-plane protons are about 10 G. Thus, the total spectral width of such a substituted cyclohexadienyl radical is between 110 and 130 G. It should be mentioned that the ESR peaks of the $\text{CH}_2\text{N}^\cdot$ ($a_{\text{H}} = 88$ G) radical [20] are sometimes weakly apparent (Fig. 2).

Finally, it is noteworthy to remark that the radicals found in this work are similar to those observed after radiolysis of aromatic hydrocarbon monocrystals at 77 K [21] in which radicals of the phenyl type or of the cyclohexadienyl type are formed.

3.3. Chemiluminescence intensity versus nitrogen atom concentration

3.3.1. Qualitative observations

Whatever the nature of the chemiluminescence spectrum — either the guest phosphorescence or a radical fluorescence — the chemiluminescence intensity exhibits a variation which parallels that of the nitrogen afterglow intensity, at least for nitrogen pressures below 10 Torr. At higher pressures the heating effect of the nitrogen flow on the temperature of the hydrocarbon surface becomes significant. An interesting conclusion arises from the following experimental facts.

(1) The chemiluminescence intensity, which reaches its maximum immediately after the condensation of the hydrocarbon on the cold finger, slowly decreases with time; at the same time, the ESR signals slowly increase.

(2) A few seconds after the condensation of the hydrocarbon on the cold finger, even though hardly any ESR signal can be detected, the chemiluminescence intensity already exhibits a variation which parallels that of the nitrogen atom concentration.

We are then forced to conclude that the limiting level for the chemiluminescence intensity is neither the radical concentration nor the guest concentration. Furthermore, a slow destruction reaction apparently competes with the chemiluminescence emission.

3.3.2. Quantitative investigation

We studied the intensity I of the chemiluminescence as a function of the nitrogen atom concentration $[\text{N}]$ for two different chemiluminescences:

(i) the naphthalene phosphorescence ($\lambda_{0-0} = 460$ nm) with the naphthalene- h_8 -benzene polycrystal; (ii) the *p*-methylbenzyl radical fluorescence ($\lambda_{0-0} = 465$ nm) with the pure *p*-xylene polycrystal. Two independent methods are employed for both chemiluminescences: the ESR method and the optical method. In both methods the same convenient variable parameter, the active nitrogen pressure, is used.

For the ESR method the set-up is modified as follows: the cold finger is now placed about 20 cm downstream from the ESR cavity, the quartz tube being directly between the ESR cavity and the cold finger. The total chemiluminescence emission (without monochromator) is focused on the photomultiplier. For both chemiluminescences we have

$$I_{\text{total}} \propto [N]^{2.2 \pm 0.2} \quad (2)$$

The principle of the optical method is to measure the intensity of the chemiluminescence as a function of the intensity I_{L-R} at 293 K of the Lewis-Rayleigh nitrogen afterglow at 293 K. This method is based on the square dependence of I_{L-R} on the nitrogen atom concentration, which has been established by Golde and Thrush [22]. However, since the spectrum of the afterglow changes from 295 to 77 K [22 - 25], it proved necessary to study the intensity of the afterglow at 77 K (*i.e.* around the cold finger) as a function of the intensity of the afterglow at 295 K. In practice, this is achieved as follows.

(1) With the bare cold finger (without hydrocarbon) at 77 K, two monochromators and photomultipliers monitor the intensity of the afterglow at 295 K (10 cm upstream from the cold finger) and at 77 K (around the cold finger). Each monochromator selects the strongest band of the $\Delta v = 4$ sequence of the First Positive system of nitrogen (11 \rightarrow 7 for 295 K, 12 \rightarrow 8 for 77 K). Even though the vibrational population is strongly affected by the temperature (Fig. 3), the following strict equality is preserved:

$$I_{12 \rightarrow 8 \text{ at } 77 \text{ K}} = (I_{11 \rightarrow 7 \text{ at } 295 \text{ K}})^{1 \pm 0.02} \quad (3)$$

This result suggests that the recombination of nitrogen atoms on a Pyrex surface at 77 K gives rise to an afterglow the intensity of which is proportional to $[N]^2$.

(2) The hydrocarbon mixture is then condensed on the cold finger and the intensity I_{0-0} of the 0-0 band of the chemiluminescence spectrum is recorded as a function of I_{L-R} at 295 K. For both the radical fluorescence and the naphthalene phosphorescence, the result obtained is (Fig. 4)

$$I_{0-0} = (I_{L-R \text{ at } 295 \text{ K}})^{0.96 \pm 0.05} \quad (4)$$

From eqns. (3) and (4) we thus derive that

$$I_{0-0} = [N]^{1.9 \pm 0.05} \quad (5)$$

Finally, both the ESR method and the optical method show that the chemiluminescence intensity roughly exhibits a square dependence on the nitrogen atom concentration. In principle, the optical method should be more reliable since the ESR signal monitors the concentration of all the nitrogen atoms

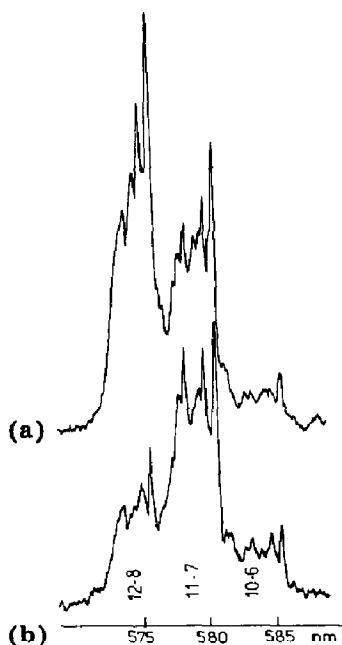


Fig. 3. Comparison of the relative intensities of three $\Delta v = 4$ bands of the Lewis-Rayleigh nitrogen afterglow at (a) 77 K and (b) 295 K.

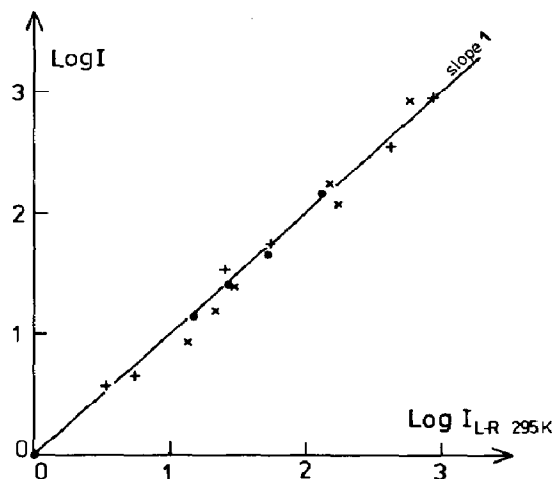


Fig. 4. Variation of the various chemiluminescence intensities I with the intensity of the 11-7 band of the nitrogen afterglow at 295 K: ●, 12-8 band of the nitrogen afterglow at 77 K; +, 0-0 band of the fluorescence of the *p*-methylbenzyl radical; x, 0-0 band of the naphthalene phosphorescence.

flowing through the cavity whereas the intensity of the Lewis-Rayleigh afterglow at 77 K derives mainly from the recombination of nitrogen atoms on the cold surface.

3.4. Summary of the experimental results

The experimental results described here may be summarized as follows.

- (1) Active nitrogen is able to populate the first triplet state of an aromatic guest, *i.e.* either a $\pi\pi^*$ or an $n\pi^*$ triplet state.
- (2) The guest phosphorescence is observed if the host is polycrystalline but is absent if the host is glassy.
- (3) With a methyl-substituted benzene derivative (as a host or as a guest) the corresponding benzyl-type radical fluorescence is emitted.
- (4) ESR spectroscopy shows that hydrogen atoms are formed during the chemical attack by active nitrogen.
- (5) Deferred luminescences are observed after the reaction of active nitrogen.

4. Interpretation and discussion

4.1. Population of the emitting states

The present spectroscopic and kinetic results can be accounted for on the basis of the following mechanism.

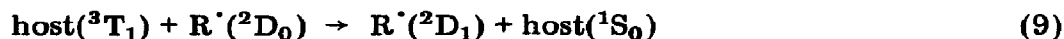
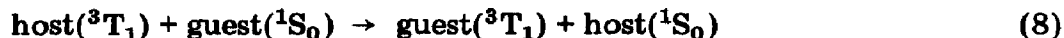
(1) The first step involves two-body recombination of nitrogen atoms on the cooled hydrocarbon surface:



(2) This is followed by triplet energy transfer to the host triplet exciton (usually benzene):



(3) The third step is the trapping of the triplet exciton energy by a low-lying excited state, *i.e.* by the guest triplet state or by a radical R[•] doublet state:

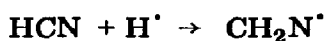
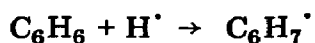
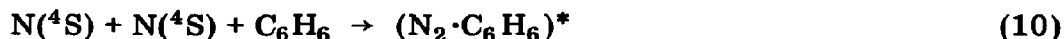


(4) The last step is either phosphorescence of the guest or fluorescence of the radical.

The various steps of this mechanism are supported by the following considerations: (i) the triplet state $^3\Sigma_u^+$ of nitrogen is already well known as a very efficient triplet energy donor, both in the gas phase [22 - 24] and in matrices at 4.2 K [1]; (ii) although triplet \rightarrow doublet energy transfers are not very common [26], it is well established that the $^3\Sigma_u^+$ electronic state of nitrogen is able to populate the excited doublet states of NO or CN for example [22 - 24].

4.2. Formation of the hydrocarbon free radicals

The experimental results lead to the conclusion that the radicals observed are characteristic of the host and not of the guest. We shall only discuss the results obtained when benzene is used as a host since benzene has been the subject of the most extensive investigations. The radicals identified ($\text{C}_6\text{H}_7^\cdot$, $\text{CH}_2\text{N}^\cdot$ and possibly $\text{C}_6\text{H}_5^\cdot$) are typical of two frequently observed chemical reactions of active nitrogen with hydrocarbons: hydrogen atom production [3, 4] and the inclusion of nitrogen into the molecule [23]. Furthermore, we have reported elsewhere [27] the formation of benzonitrile during the reaction of active nitrogen with pure benzene, in agreement with the results of Arconovich and Mikhailov [28]. The experimental results may be accounted for by the following sequence of reactions:



The formation of a transient highly energetic complex (reaction (10)) before decomposition is often postulated to explain the kinetics or the nature of the reaction products in the reactions of active nitrogen [23].

4.3. Origin of the deferred luminescences

The observation of deferred luminescences after the reaction of active nitrogen is a puzzling phenomenon. Allen [29] has observed an active-nitrogen induced ionization during the reaction with sodium salts. As outlined earlier, deferred luminescences (isothermal luminescences and thermoluminescences) are commonly observed after radiolysis or photoionization of glassy matrices containing aromatic solutes [8 - 11]. The well-known properties of these deferred luminescences are as follows.

(1) The spectrum of the deferred luminescence is the solute phosphorescence, with sometimes a small contribution from the solute fluorescence.

(2) The deferred luminescence can be stimulated by irradiation in the visible or the IR, or by heating (thermoluminescence).

(3) The widely accepted interpretation is the recombination of charged species (electrons or anions with cations).

The deferred luminescences observed in the present work exhibit exactly the same characteristics as those observed following radiolysis; if the same interpretation is to be invoked, an ionization — either of the guest or of the host — induced by active nitrogen must occur. In this hypothesis an energy of about $75\,000\text{ cm}^{-1}$ is required with the benzonitrile–benzene polycrystal (the ionization potentials given in Fig. 5 were taken from ref. 30).

Thus, a direct ionization (via reaction (7)) of the hydrocarbon induced by the triplet nitrogen in its low vibrational levels is excluded. In contrast, the energy available in reaction (10) (approximately $80\,000\text{ cm}^{-1}$) is higher than the ionization potential of benzene.

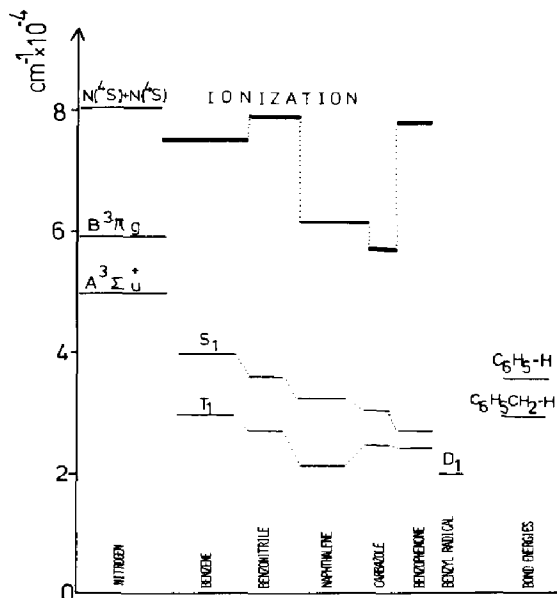


Fig. 5. Gas phase ionization potentials and energies of the first excited electronic states of nitrogen, benzene, benzonitrile, naphthalene, carbazole and benzophenone, together with the energy of the excited doublet states of the benzyl radical and the energies of the $C_6H_5CH_2-H$ and C_6H_5-H bonds.

An alternative interpretation of the ionization has been proposed by Hellner and Vermeil [31] to explain their observation of thermoluminescences after vacuum-UV photolysis: the electronic energy is supposed to be trapped by crystals defects during the photolysis.

Finally, it is noteworthy to compare the present observations with recent work [32] on the reaction of the oxygen atom with acetylene; both an ionization and a chemiluminescence of CO are shown to occur. Furthermore, the rate of chemionization is proportional to the square of the oxygen atom concentration and the same complex between acetylene and oxygen is considered to produce both the chemiluminescence and the chemionization.

5. Conclusions

The reaction of active nitrogen with a variety of mixed host-guest polycrystals at 77 K exhibits three salient features: (i) emission of luminescences, mostly characteristic of the guest; (ii) formation of hydrocarbon free radicals; (iii) emission of deferred luminescences. Most of the experimental observations can be accounted for by two-body recombination of the nitrogen atom on the cold surface and subsequent energy transfer.

It is noticeable that these characteristics of the reaction of active nitrogen with hydrocarbons are typical of what happens through some processes involving a high excitation energy. Since the energy of the triplet state ${}^3\Sigma_u^+$ ($v = 0$) of nitrogen is about $50\,000\text{ cm}^{-1}$ (6.4 eV), the guest molecule may be excited into its upper triplet states (see Fig. 5) after the triplet \rightarrow triplet energy transfer; the same states are reached on vacuum-UV photolysis or after triplet \rightarrow triplet absorption in biphotonic reactions. Both photophysical processes are usually followed by deferred luminescences and sensitized decomposition of the solvent, similar to those occurring during the active nitrogen reaction. Apparently, the triplet state ${}^3\Sigma_u^+$ of nitrogen has the same effect as the two successive steps in a two-quanta photolysis. Finally, the radicals detected in the present work (cyclohexadienyl, phenyl or benzyl type) are commonly observed on radiolysis [21], or after flowing hydrocarbons through high frequency discharges [33].

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References

- 1 E. Faure, *Thèse*, Lyon, 1974.
F. Valadier, E. Faure, R. Bergeron and J. Janin, *C.R. Acad. Sci.*, 265 (1967) 1432.
- 2 O. Dessaux, *J. Chim Phys. Phys.-Chim. Biol.*, 67 (1970) 1137; *Thèse N° AO 2829*, Paris, 1968.

- R. Demary and O. Dessaux, *J. Chim. Phys. Phys.-Chim. Biol.*, 71 (4) (1974) 555.
- 3 A. Forchioni and C. Chachaty, *C.R. Acad. Sci.*, 264 (1967) 637.
- 4 R. Minkwitz and F. W. Froben, *Chem. Phys. Lett.*, 39 (1976) 473.
F. W. Froben, *J. Phys. Chem.*, 78 (1974) 2047.
F. W. Froben, *Ber. Bunsenges. Phys. Chem.*, 82 (1978) 8.
- 5 V. D. Shatrov, O. F. Pugachev and E. B. Gordon, *Opt. Spectrosc. (U.S.S.R.)*, 36 (1974) 413.
- 6 P. Devolder, *Spectrochim. Acta, Part A*, 36 (1980) 783.
- 7 A. Branciard-Larcher, E. Migirdicyan and J. Baudet, *Chem. Phys.*, 2 (1973) 95.
P. M. Johnson and A. C. Albrecht, *J. Chem. Phys.*, 48 (1968) 851.
- 8 F. Kieffer and M. Magat, *Actions Chim. Biol. Radiat.*, 12 (1969) 135.
- 9 L. Kevan, *Actions Chim. Biol. Radiat.*, 15 (1972) 81.
W. H. Hamill, *Radical Ions*, Interscience, New York, 1968, 321.
- 10 K. Yoshinaga, N. Yamamoto and H. Tsubomura, *J. Lumin.*, 6 (1973) 179.
W. M. McClain and A. C. Albrecht, *J. Chem. Phys.*, 43 (1965) 465.
H. Moeckel, J. Yuen and L. Kevan, *Int. J. Radiat. Phys. Chem.*, 7 (1975) 251.
D. Muller, M. Ewald and G. Durocher, *Can. J. Chem.*, 52 (1974) 3707.
- 11 B. Brocklehurst, R. D. Russel and M. I. Savadatti, *Trans. Faraday Soc.*, 65 (1966) 1129.
- 12 Kh. S. Bagdasaryan, *Kinet. Catal. (U.S.S.R.)*, 8 (1967) 920.
P. Cordier, J. F. Delouis, F. Kieffer, C. Lapersonne and J. Rigaut, *C.R. Acad. Sci., Sér. C*, 279 (1974) 589.
F. Kieffer, C. Lapersonne-Meyer and J. Rigaut, *Int. J. Radiat. Phys. Chem.*, 6 (1974) 79.
- 13 V. V. Voevodski, *Actions Chim. Biol. Radiat.*, 6 (1963) 71.
S. I. Ohniski, T. Tanet and I. Nitta, *J. Chem. Phys.*, 37 (1962) 2402.
- 14 P. H. Kasai, E. Hedaya and E. B. Whipple, *J. Am. Chem. Soc.*, 91 (1969) 4364.
- 15 J. E. Bennet, B. Mile and A. Thomas, *Proc. R. Soc. London, Ser. A*, 293 (1966) 246.
- 16 P. Devolder, P. Bourlet and O. Dessaux, *C.R. Acad. Sci., Sér. C*, 277 (1973) 65.
- 17 D. Campbell and D. T. Turner, *Can. J. Chem.*, 45 (1967) 881.
D. Campbell, M. C. R. Symons and G. S. P. Venna, *J. Chem. Soc. A*, (1969) 2480.
- 18 T. Matsuyama and H. Yamaoka, *Chem. Phys. Lett.*, 57 (1978) 269, and references cited therein.
- 19 S. Digregorio, M. B. Yim and D. E. Wood, *J. Am. Chem. Soc.*, 95 (1973) 8455.
- 20 N. V. Vugman, M. F. Elia and R. P. A. Muniz, *Mol. Phys.*, 30 (1975) 1813.
D. Banks and W. Gordy, *Mol. Phys.*, 26 (1973) 1555.
- 21 T. Okubo, N. Itoh and T. Suita, *Mol. Cryst. Liq. Cryst.*, 6 (1969) 227.
T. Chong and N. Itoh, *J. Phys. Soc. Jpn.*, 35 (1973) 513.
U. R. Bohme and G. W. Jesse, *Chem. Phys. Lett.*, 3 (1969) 329.
R. W. Jennings and L. K. Wilson, *Mol. Cryst. Liq. Cryst.*, 17 (1972) 315.
A. Cadoux and M. Martin-Bouyer, *J. Chim. Phys. Phys.-Chim. Biol.*, 70 (1973) 679.
- 22 M. F. Golde and B. A. Thrush, *Rev. Prog. Phys.*, 36 (1973) 1285.
- 23 A. N. Wright and C. A. Winkler, *Active Nitrogen*, Academic Press, New York, 1968.
R. Brown and C. A. Winkler, *Angew. Chem.*, 9 (1970) 181.
- 24 J. Anketell and R. W. Nicholls, *Rev. Prog. Phys.*, 33 (1970) 269.
- 25 V. H. Kurzweg and H. P. Broida, *J. Mol. Spectrosc.*, 3 (1959) 388.
- 26 K. R. Nagvi, H. Staerk and T. Gillbro, *Chem. Phys. Lett.*, 49 (1977) 160.
K. R. Nagvi and U. P. Wild, *Chem. Phys. Lett.*, 41 (1976) 570.
- 27 P. Devolder, *J. Lumin.*, 21 (1980) 177.
- 28 P. M. Arconovich and B. M. Mikhailov, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sic.*, 5 (1956) 541; 6 (1956) 707.
- 29 E. R. Allen, *J. Photochem.*, 9 (1978) 159.
- 30 B. S. Freiser and J. L. Beauchamp, *Chem. Phys. Lett.*, 42 (1976) 380.
J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley-Interscience, New York, 1970.
V. I. Vedeneyev, *Bond Energies, Ionization Potentials and Electron Affinities*, Edward Arnold, London, 1966.
- 31 L. Hellner and C. Vermeil, *J. Mol. Spectrosc.*, 62 (1976) 313; 60 (1976) 71.

- 32 C. Winckler, M. P. Gardner and K. B. Bayes, *J. Phys. Chem.*, 81 (1977) 2137.
33 S. Kikkawa, M. Nomura and Y. Morita, *Chem. Lett.*, (1974) 1337.
M. Bigwood, A. Delaby and S. Boue, *Nouv. J. Chim.*, 1 (1978) 883.

Note added in proof

Recent measurements with increased sensitivity confirm that the deferred luminescence emitted by the naphthalene-benzene mixed polycrystal is indeed the naphthalene phosphorescence.