Gamma-Ray Induced Luminescence of Silica Gel

II. Luminescence Occurring on Adsorption of Gases: Radiosorptionluminescence

K. Breitkreutz *, P. Kirmaier, and J. G. Rabe
Hahn-Meitner-Institut für Kernforschung Berlin GmbH, Ber. Strahlenchemie, Berlin, Germany

(Z. Naturforsch. **30 a**, 170–174 [1975]; received December 14, 1974)

Luminescence observed on adsorption of gases and vapours (RSL) on silica gel previously exposed to γ-rays has been investigated. The dependence of RSL intensity on absorbed radiation dose and degassing temperature of the gel prior to irradiation parallels the dependence of radiothermoluminescence (RTL) intensity: A limiting value is reached around 1 Mrad and the intensity increases steeply on raising the degassing temperature. The RSL intensity is largest on adsorption of H_2 and decreases in the order H_2; O_2; N_2O; N_2; He. The stronger the RSL effect, the more is the subsequent measured RTL reduced. The RSL emission spectrum has a maximum at 450 nm and is identical with the spectrum of RTL. In some cases bands at longer wavelengths have been observed. The RSL decays with hyperbolic kinetics which may be related to the logarithmic rate of adsorption as given by the Elovich equation. The results are discussed in terms of detrapping of charges, in this case stimulated by adsorption, and the recombination of carriers leading to excitation of luminescent centers as in RTL. The emission bands at longer wavelengths are thought to involve electron transfer from interacting molecules neutralizing holes trapped in the solid.

1. Introduction

Numerous reactions of substrates at the surface of solids have been reported to occur only when the solids (usually oxides or halides) were previously subjected to ionizing radiation [1]. To quote a few examples we mention chemisorption [2, 3] and decomposition [4, 5] of substrate molecules at γ-irradiated silica gel. The results indicate that the reactions are associated with radiation produced defects, i. e. trapped electrons and holes. Such reactions may therefore be expected to interfere with luminescence which results from the recombination of charges yielding excited luminescence centers. Experimental verification for γ-irradiated silica gel is presented in the preceding paper (referred to as I). Considering the quantity of energy liberated in for instance an adsorption process, it seems quite probable that the energy suffices to provide the activation energy for detrapping of charges. A hint is obtained from a study of γ-irradiated sodium chloride where the occurrence of adsorbate decomposition was found to be less frequent than the concomitant disappearance of F-centers [6].

We investigated, therefore, whether the interaction of substrate molecules with an irradiated surface is accompanied by the emission of light. Preliminary accounts of the observed luminescence with γ-irradiated silica gel have been given [7, 8]. A similar phenomenon with irradiated silica-alumina gel has been reported by Hentz and Ziemecki [9]. In contrast to radiothermoluminescence (RTL), the luminescence stimulated by adsorption is called radiosorptionluminescence (RSL).

* Now: Bundesanstalt für Materialsprüfung, Berlin.
Reprint requests to Dr. J. G. Rabe, Hahn-Meitner-Institut für Kernforschung, *D-1000 Berlin 39*, Postfach 390128.

2. Experimental Section

The silica gel, "HR extrapure acc. to Stahl", was the same as that used in Part I. Except for the tube containing the gel, which was a quartz tube of 3 mm internal diameter in contrast to the 0.6 mm pyrex tube used for RTL, the general experimental procedure was as described in I. Details of the set-up for measurement of luminescence are given in I. For measurements at room temperature sometimes a simplified version of the device was used. For fast decaying RSL the spectral distribution of emission was measured by using a circular filter (Barr and Stroud CGS 2, 400 – 700 nm) which could be rotated with high speed. The photomultiplier output was then recorded by a fast responding light beam oscillograph (Oscillofil from Siemens).

3. Results

3.1. Observation of Radiosorptionluminescence (RSL)

Luminescence (RSL) is observed when silica gel previously outgassed at 800 °K to 10^{-5} Torr and irradiated at room temperature to 1 Mrad is exposed to various gases or vapours. In a dark room light emission can be seen with the naked eye. A typical signal recorded as the photomultiplier output accompanying adsorption of hydrogen versus

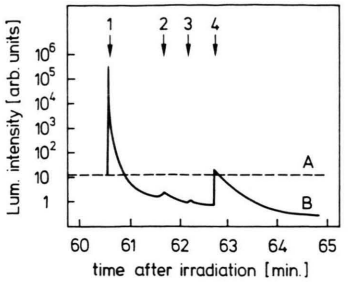

Fig. 1. Luminescence accompanying admission of hydrogen to γ-irradiated silica gel as a function of time (room temperature; radiation dose: 10^6 rad). A: Luminescence of gel under vacuum; B: Luminescence on hydrogen admission. Addition of molecules per gram gel: 1; 2; 3; -5×10^{18} molecules H_2. 4; -1.5×10^{21} molecules H_2.

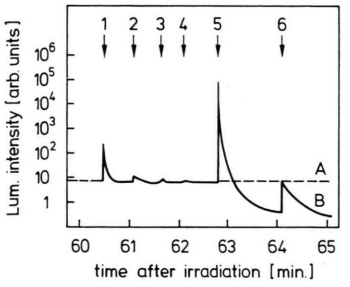

Fig. 2. Luminescence accompanying admission of nitrogen and hydrogen to γ-irradiated silica gel as a function of time (room temperature; radiation dosé 10^6 rad). A: Luminescence of gel under vacuum; B: Luminescence on nitrogen and hydrogen admission. Addition of molecules per gram gel: 1; 2; 3; -5×10^{18} molecules N_2. 4; -1.5×10^{21} molecules N_2. 5; 5×10^{18} molecules H_2. 6; $-1{,}5 \times 10^{21}$ molecules H_2.

time is shown in Figure 1. Already a small amount of gas (for H_2 corresponding to about 0.2% surface coverage) causes an increase of the intensity by several orders of magnitude. There is a decay in intensity to a value lower than the background intensity originating from thermo luminescence of a sample irradiated at room temperature (Fig. 3 in I). Addition of a second portion of the same gas has but a small effect. The maximum RSL intensity decreases in the order $H_2 > O_2 > N_2O > N_2 > CH_4 > He$; Ar. The noble gases do not affect RTL measured subsequent to their addition, whereas hydrogen, which induces strong RSL, to the contrary suppresses RTL almost completely. When first a less effective gas is admitted, the subsequent addition of a second more effective gas causes RSL again. This is shown in Fig. 2 for the admission of hydrogen subsequent to nitrogen. Another example – hydrogen following oxygen adsorption – is pictured in Reference [7]. If, however, RSL is initiated by hydrogen adsorption, subsequent admission of the less effective oxygen failed to produce RSL. The light emitted during RSL does not exceed 10% of the RTL reduction involved.

The RSL emission spectra consist of a band peaking at 450 nm and is identical with the band observed for RTL. Since irradiated gels exhibit absorption spectra, Hentz and Ziemecki [9] have discussed the possibility that the observed luminescence spectrum may not correspond to the emission spectrum on account of self absorption. This effect, however, cannot be important in the present case because the luminescence spectrum did not change in the heavily irradiated gel although optical absorption had strongly increased. Various vapours (water, diacetyl, dimethylaniline and tetranitromethane) induced the same 450 nm emission except that the RSL intensity rose more slowly due to the slower diffusion through the gel. Howwever, there was an additional emission band at 620 nm. Occasionally this band was also observed during hydrogen adsorption.

RSL has also been observed with γ-irradiated magnesia and silica-alumina gel. Although not studied in detail, the observations on silica-alumina gel (kindly provided by R. Hentz) seem in qualitative agreement with those of Hentz and Ziemecki [9]; namely with hydrogen and some organic compounds RSL emission at wavelengths different from RTL emission is observed. Contrary to silica gel, RSL induced by O_2 or N_2O adsorption is of minor importance (the yield is only a few per cent of the RSL induced by H_2 and escaped detection by Hentz [9]).

3.2. *Influence of Radiation Dose and Thermal History of the Gel*

The dependence of RSL intensity on radiation dose and on the degassing temperature of the gel prior to irradiation parallels the dependence of RTL intensity (Figs. 4 and 6 in I). The intensity increases linearly with dose reaching saturation at around 1 Mrad; an increase of degassing temperature results in an increased RSL intensity. Because RTL has decayed in a hyperbolic fashion with time, the RSL induced by adsorption is reduced in intensity; but even in samples heated to 373 °K in order to remove RTL, subsequent adsorption of oxygen at room temperature does initiate RSL. However,

spectral analysis revealed the absence of the 450 nm emission peak and the occurrence of a band peaking at 500 – 550 nm. Furthermore, in the subsequent addition of hydrogen the RSL at 620 nm now clearly dominates the 450 nm emission.

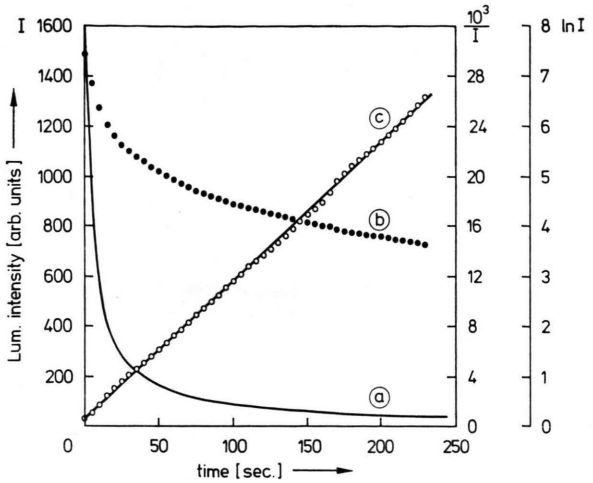

Fig. 3. Decay kinetics of the luminescence occurring on admission of hydrogen to γ-irradiated silica gel at 77 °K. Plots as a function of time of (a) luminescence intensity, (b) ln of luminescence intensity assuming first order decay and (c) reciprocal of luminescence intensity assuming hyperbolic dependence.

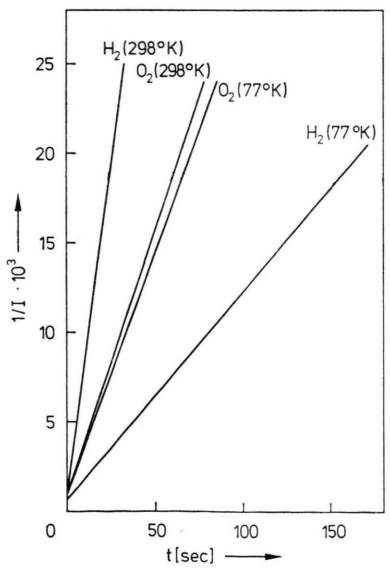

Fig. 4. Decay of luminescence on gas adsorption at γ-irradiated silica gel, assuming hyperbolic dependence (Fig. 3).

In order to elucidate whether RSL could be initiated at temperatures lower than the temperature required for thermal stimulation (RTL) the following experiment was performed: Samples irradiated at 77 °K were heated to 153 °K and the RTL allowed to decay at this temperature. After recooling to 77°, both oxygen and hydrogen, respectively, were admitted causing RSL. On heating, practically no RTL could be observed which without gas adsorption would have started at 153 °K. Even when samples irradiated at room temperature were cooled to 77 °K, strong RSL could be observed on addition of both gases. Apparently, adsorption of certain gases stimulated light emission (RSL) which thermally (RTL) occurs at temperatures 150 – 200° higher.

3.3. Kinetic Studies of RSL

The decay of RSL initiated by adsorption of hydrogen and oxygen has been measured at 77 °K and 298 °K, respectively. A typical decay curve, in this case the RSL decay observed at 77 °K on adsorption of hydrogen, is shown in Figure 3(a). The decay could not be fitted to a first order process as is seen from the plot of ln intensity versus time (b). A fair fit is obtained with the reciprocal of the intensity plotted versus time (c). Similar treatment of the data obtained with hydrogen at 298 °K and with oxygen at 77 °K and 298 °K likewise exhibited a hyperbolic decay with the functional dependence of $I(t) \propto 1/(\alpha+\beta t)$, where α and β are constants. In Fig. 4 the decay of hydrogen and oxygen induced RSL is shown for comparison. It will be noted that the decay rate for oxygen induced RSL does hardly change with temperature. In contrast, the hydrogen induced RSL decays with a rate increasing considerably when the temperature is raised.

4. Discussion

Of the two possible explanations for the observed luminescence, (a) radiative transition within an adsorbed molecule and (b) emission from a luminescent center of the solid, the first can be rejected due to the observation of identical emissions for a great variety of gases and vapours. The identical emission found for RTL and RSL suggests that the same transitions in a luminescent center of the solid are involved. Since in RTL the excitation of a luminescent center is thought to result from the recombination of electrons with holes thermally released from traps, it may be proposed that in RSL the recombination is stimulated by adsorption of molecules. It

is known that hydrogen and oxygen become irreversibly adsorbed when admitted to silica gel previously subjected to γ-irradiation [3]. It should be noted that nitrogen and the noble gases, expected to interact with the irradiated surface by Van der Waals forces only, are inefficient in producing RSL when compared with hydrogen or oxygen.

The decay of luminescence (Fig. 3) is described by the hyperbolic relation

$$1/I(t) - 1/I_0 = k\,t\,. \qquad (1)$$

The luminescence intensity $I(t)$ has the functional dependence

$$I(t) \propto 1/(\alpha + \beta\,t)$$

where α and β are constants. If we make the reasonable assumption that the luminescence is initiated by adsorption, we may expect that, provided adsorption is the rate determining step, the rate of radiative transitions $-(\mathrm{d}n/\mathrm{d}t) = I(t)$ is proportional to the rate of adsorption $\mathrm{d}q/\mathrm{d}t$. Then

$$\mathrm{d}q/\mathrm{d}t \propto 1/(\alpha + \beta\,t) \qquad (2)$$

which on integration gives

$$q \propto C + (1/\beta)\ln(\alpha + \beta\,t) \qquad (3)$$

where C is a constant. From Eq. (3) one obtains

$$(\alpha + \beta\,t) \propto e^{\beta q} \cdot e^{-\beta C} \qquad (4)$$

the reciprocal of which yields on replacing $e^{\beta C}$ by a constant a and considering Eq. (2)

$$\mathrm{d}q/\mathrm{d}t \propto a \cdot \exp(-\beta\,q)\,. \qquad (5)$$

Equation (5) gives the rate of adsorption as a function of q, the amount adsorbed at time t, with a and β being constants. It is the Elovich equation known to be satisfactorily applicable to most chemisorption data [10]. Although not investigated specifically, it is of interest to point out that the observed decay kinetics of RSL is in accordance with chemisorption kinetics. The surplus energy of the transition state in a chemisorption process can apparently be spent for the release of charges from traps. Traps filled on irradiation at room temperature are about 0.7 eV in depth (Part I). That RSL could still be initiated by adsorption at 77 °K may be explained by the fact that already a surplus energy around 20 kcal mole^{-1} is of the order of the trap depth.

Defining the quantum efficiency as the fraction of charge recombinations leading to radiative emissions, it must be admitted that the RSL efficiency is considerably smaller than the RTL efficiency. At present it cannot be decided whether this is due to competing reactions, as for instance charge transfer reactions between solid and adsorbate, or alternatively, is due to nonradiative desactivation which, perhaps, is favored by the presence of adsorbate molecules.

The occurrence in RSL of wavelengths not encountered in RTL indicates that in addition to the recombination of charges leading to a 450 nm emission, specific reactions of the adsorbate molecules are taking place. The bands observed at 520 – 550 nm and at 620 nm are tentatively attributed to the neutralization of holes by electrons donated by the previously formed O_2^- [8] and by hydrogen or organic compounds, respectively, as proposed by Hentz [9]. Support is obtained from the observation that these bands become predominant when first RTL (450 nm) is removed by gentle heating and then RSL is initiated.

With respect to the RSL emission found with silica-alumina gel, the absence of the RTL wavelengths indicate the prevalence of a neutralization mechanism in contrast to the recombination mechanism operative in silica gel. It should be mentioned that both gels differ with respect to their reactivity towards electron acceptors. On irradiated silica gel, O_2 [8, 11], SO_2 [11, 12] and CO_2 [11, 12] do react, concomitantly affecting the trapped electrons, whereas on irradiated silica-alumina gel they are unreactive [13].

Failure to produce RTL subsequent to hydrogen adsorption and to induce – after H_2 adsorption – RSL by addition of any other gas both suggest that hole centers are necessary for luminescence. Nevertheless, in the case of oxygen the anion-radical O_2^- is formed [8] and the absence of RSL thus proves that this charge transfer does not yield luminescence.

The occurrence of luminescence on adsorption of gases on solids which – contrary to the present study – were not previously subjected to ionizing radiation has been reported by several laboratories. Various gases were found to initiate luminescence with silicium [14], tungsten [15], zinc oxide [16], magnesia [17, 18], and nickel oxide [17]. It is of interest to compare the basic results. It should be mentioned first that for silica gel we detected luminescence without prior irradiation but its intensity was lower by several orders of magnitude when compared to RSL. There is agreement that the luminescence de-

cay has an hyperbolic time dependence. Also, all agree that luminescence is initiated by the surplus energy of adsorption. Different opinions exist on the origin of luminescence. Luminescence of the oxygen-silicium system is attributed to a gas-phase emission, whereas emission from the solid occurs in the oxygen-zinc oxide [16], oxygen-magnesia [18] and the present gas-irradiated silica gel system. As for the mechanisms, without irradiation the energy liberated on adsorption is thought to excite luminescence, whereas with the solid being irradiated excitation results from charge recombination and/or neutralization as outlined above.

Acknowledgement

We wish to thank the Deutsche Forschungsgemeinschaft for financial support.

[1] E. H. Taylor, Adv. Catalysis **18**, 111 [1968].
[2] H. W. Kohn, Nature London **184**, 630 [1959].
[3] J. G. Rabe, Int. J. Radiat. Phys. Chem. **5**, 301 [1973].
[4] E. A. Rojo and R. R. Hentz, J. Phys. Chem. **70**, 731 [1966].
[5] J. G. Rabe, B. Rabe, and A. O. Allen, J. Phys. Chem. **70**, 1098 [1966].
[6] J. G. Rabe and G. Joppien, Z. Naturforsch. **24a**, 796 [1969].
[7] J. G. Rabe and K. Breitkreutz, Z. Naturforsch. **25a**, 571 [1970].
[8] J. G. Rabe and K. Breitkreutz, Ber. Bunsenges. phys. Chem. **75**, 1123 [1971].
[9] R. R. Hentz and S. B. Ziemecki, J. Phys. Chem. **74**, 3552 [1970].
[10] M. J. D. Low, Chem. Rev. **60**, 267 [1960].
[11] Y. Yamada, A. Hasegawa, and M. Miura, Bull. Chem. Soc. Japan **42**, 1836 [1969].
[12] P. K. Wong and J. E. Willard, J. Phys. Chem. **73**, 2226 [1969].
[13] R. R. Hentz and D. K. Wickenden, J. Phys. Chem. **73**, 817 [1969].
[14] L. E. Brus and J. Comas, J. Chem. Phys. **54**, 2771 [1971].
[15] B. McCarroll, J. Chem. Phys. **50**, 4758 [1969].
[16] W. D. Schulze and J. Scheve, Z. anorg. allgem. Chemie **377**, 113 [1970].
[17] S. Z. Roginski and Yu. N. Rufov, Kinetika i Kataliz **11**, 383 [1970].
[18] Yu. N. Rufov and S. K. Bokova, Khim. Vys. Energ. **6**, 353 [1972].