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Continuous Irradiation Induced Luminescence from Benzophenone, 4,4′-Dichlorobenzophenone, and 4-(Dimethylamino)benzaldehyde in Solid Environments and Its Pressure Dependence[†]

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We report a strong emission change induced by continuous light irradiation in two ketones, benzophenone and 4,4′-dichlorobenzophenone, and an aldehyde, 4-(dimethylamino)benzaldehyde, in their crystalline state as well as dissolved in solid polymers. With prolonged laser irradiation, a time evolution of the emission intensity shows complex features, but two clear competing trends can be distinguished: an increase and/or decrease of the emission intensity. It is shown that these trends may be a result of creation of either an emissive or a nonemissive species. The relative importance of these two pathways is significantly dependent on the type of medium and external pressure. The most characteristic feature of these dependencies is the fact that in crystalline environments, in contrast to polymers, the emission intensity at all pressures only decreases. A kinetic model is developed that assumes the lowest triplet state as the origin of the high photoreactivity of these molecules, causing their emission intensity change. This model embraces the observations either in crystalline or polymeric environments and is solved for two limiting cases: a predominance of the hydrogen abstraction reaction from the polymer or a predominance of the ionization due to biphotonic excitation of the triplet state. These processes are assumed responsible, respectively, for the creation of emissive and nonemissive photoproducts. By comparison of the model with experimental results some of the parameters involved in these processes are extracted and their pressure dependence can be predicted.

1. Introduction

The present paper is a continuation of our investigations of pressure and light induced effects on luminescence of molecules with nonbonding electrons dissolved in solid media.[1−4] The general interest in this class of molecules has stemmed mainly from their prolific triplet state features providing a variety of excellent examples for that kind of photophysical and photochemical studies like singlet−triplet intersystem crossing, triplet−triplet annihilation, energy transfer and migration, triplet-state absorption, and triplet-state photoreactivity via the hydrogen abstraction and/or α-cleavage reactions. As we have shown, for some of these processes, they can be significantly perturbed under external hydrostatic pressure providing new information inaccessible at atmospheric pressure.

Among the processes studied the photoinduced reactivity of the aromatic carbonyls has attracted special attention since these compounds possess two features common for highly photoreactive molecules, i.e. a conjugated system of π electrons and a number of nonbonding electrons. A review of an extensive literature of this subject reveals that most of the previous studies have concentrated on these processes in liquid solutions (see e.g. refs 5−10). Of special interest has been the relationship between the nature of excited states and the efficiency of the photochemical reaction. It has been established that photoreactions of these compounds in liquid solutions occur through the lowest triplet state, which is of n,π* type, and are characteristic of attack by an electron deficient oxygen atom. Thus in hydrogen-donating solvents, a hydrogen abstraction from the solvent molecules may proceed, resulting in formation of two intermediates: solute and solvent molecule radicals. If these two fragments can diffuse apart or reorient with respect to each other, a variety of stable photoproducts can be formed,[11−14] and photoreduction efficiency may particularly depend on the amount of the n,π* character in the triplet state, the strength of the C−H bond in the hydrogen donor, and the distance and orientation between carbonyl and donor molecule.

By contrast, there is much less information on photoreactivity of aromatic carbonyls in solid media: polymeric,[15−19] crystalline,[20−22] and low-temperature glasses.[23,24] In these, essentially rigid, environments since diffusion of the geminate pair of radicals is markedly inhibited, the hydrogen abstraction reaction reveals, in general, lower efficiency than in liquid solutions. However, the reactivity of carbonyls, particularly ketones, in solid matrices increases when a strong excitation light from the laser is used. It has been suggested that a higher excited triplet state instead of the lowest one is involved in this case to abstract hydrogen[16] from the solvent molecules. However, in our experiments, when we employ a continuous irradiation with a moderate incident light intensity, significant changes in the emission characteristics of three carbonyls, benzophenone (BP), 4,4′-dichlorobenzophenone (DCBP), and 4-(dimethylamino)-benzaldehyde (DMABA) in solid media are observed. As we show, the character of this photoreactivity depends essentially on the type of medium and external pressure.

In the preceding paper it has been shown that the pressure-induced mixing of the n,π* and π,π* character of the lowest triplet state is responsible for significant changes of the emission intensity of BP, DCBP, and DMABA in polymeric as well as in crystalline environments. In this paper we attempt to show that the n,π* triplet state and changes of its character either by the change of the medium or pressure may also be a key of the characteristic photoreactivity of these compounds under continuous laser irradiation.

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2. Experiment

The samples and their preparation have been described in the preceding paper.[4] The light-induced experiments, either the emission or absorption, were performed in a Merrill−Bassett diamond anvil cell (DAC) at room temperature, utilizing low-fluorescence diamonds with a culet diameter of approximately 0.8 mm. The sample chamber consisted of a 0.3 mm hole drilled in a preindented Inconel gasket. The samples, approximately 50−100 μm thick, were loaded in the sample chamber along with the ruby chips used as the pressure calibrant and with mineral oil as a pressurizing medium. The 325 nm line of a He−Cd laser (5 mW, Omnichrome 56X series) was used as a source of excitation and irradiation of the sample. The output laser intensity was estimated to be 8×10^{15} photons/s and the maximum effective intensity at the surface of the sample 2 orders of the magnitude lower. In the spectra measurement experiments, the incident intensity was kept lower than 10^{12} photons/s. In the irradiation experiments the sample was exposed to the flux estimated to be about 2×10^{12} photons/s unless otherwise specified. Emission from the sample was collected in front-face mode and focused on the entrance slit of a Kratos monochromator. The detector was a cooled EMI 9558QA photomultiplier tube (PMT). A PMT signal was sent to a preamplifier followed by an amplifier discriminator and photon counter (Ortec 9301, 9302, and 9315, respectively). During continuous irradiation the emission at the chosen emission line was monitored by the above system and computer on-line with a reading interval of 2 s. The experimental setup for the UV−vis absorption measurements has been described elsewhere.[25]

3. Results

All compounds studied, both in polymeric and crystalline environments, after irradiation, exhibit significant changes in their emission and absorption spectra. The main effect of the irradiation is an increase of intensity of some absorption or emission bands and a decrease of others. Besides the changes in the intensity, changes in the shape of the spectra are also observed. These changes indicate either the disappearance of the original molecules or the creation of new photoproducts or both. Since the most spectacular changes are seen in emission, we focus mainly on the luminescence measurements. Furthermore, we show that the pressure under which the experiments are carried out and the type of matrix largely determine the features of the irradiation effect.

3.1. Influence of Irradiation on the Absorption and Emission Spectra. *3.1.1. BP and DCBP.* BP in PEMA as well as in PVCl absorbs in two regions: between ≈(24−32) × 10^3 cm^{-1} (low-energy band) and above 32 × 10^3 cm^{-1} (high-energy band). The low and high energy bands, on the basis of their pressure and medium dependence, are assigned as an S(n→π*) and an S(π→π*) transition, respectively. The high-energy band, of which only the shoulder is seen (because of low UV transmission of the diamonds), overlaps more strongly with the low-energy band as both the pressure and polarizability of the medium increase. The irradiation of a sample for a period of about 25 min increases the optical density over the entire n → π* region (see Figure 1). A new band, obtained as the difference between the absorption curve before and after irradiation, shows much stronger pressure dependence than the original n → π* transition. Over a 50 kbar range the maximum of the new peak shifts almost 2000 cm^{-1}, indicating its π,π* rather than n,π* character. The absorption intensity of the new band is also higher than that of the nonirradiated sample. Moreover, the irradiation effect is more pronounced (a stronger shift of the new peak to low energy and larger increase of the intensity) in PVCl than in PEMA.

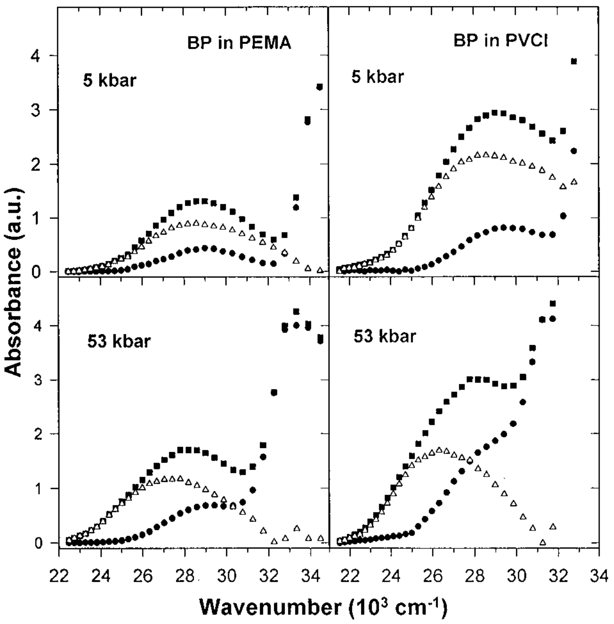

Figure 1. Absorption spectra of BP in PEMA and PVCl at 5 and 53 kbar: (●) before irradiation, (■) after irradiation for 25 min by a flux of 2 × 10^{12} photons/s, (△) difference between before and after irradiation.

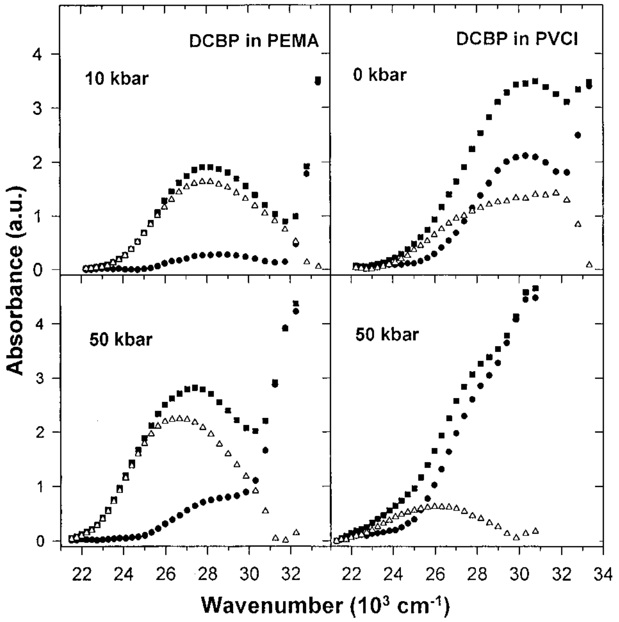

Figure 2. Absorption spectra of DCBP in PEMA at 10 and 50 kbar and DCBP in PVCl at 0 and 50 kbar: (●) before irradiation, (■) after irradiation for 25 min by a flux of 2 × 10^{12} photons/s, (△) difference between before and after irradiation.

The absorption spectra of DCBP in PEMA and PVCl (see Figure 2) upon irradiation show qualitatively the same features as BP. Some irregularities, in the case of DCBP in PVCl, in the resulting spectrum (a difference between the spectrum of irradiated and nonirradiated samples) are perhaps introduced by strong initial (with no irradiation) overlap of the high and low energy band. In all cases studied (BP and DCBP) the intensity of the light-induced absorption peak exhibits high stability over a long time at all pressures, including atmospheric.

Both BP and DCBP at atmospheric pressure show a very low emission intensity, identified as phosphorescence, with a spectrum possessing a characteristic vibrational structure. Under irradiation the spectrum loses its structure and is transformed

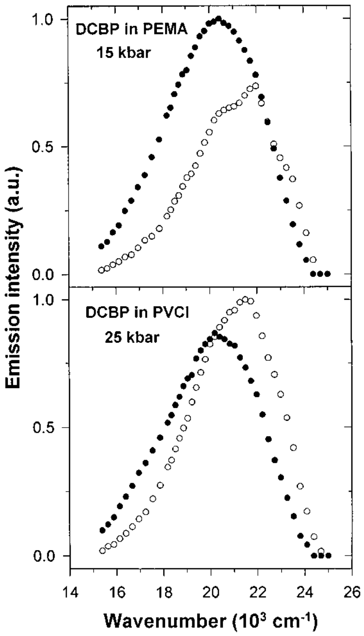

Figure 3. Emission spectra of DCBP in PEMA at 15 kbar and DCBP in PVCl at 25 kbar: (○) before irradiation and (●) after irradiation for 25 min by a flux of 2 × 10^{12} photons/s.

into a smooth curve with a high intensity. In the case of BP the maximum of the irradiated sample is approximately located at the center of the emission of the untreated sample. However, in the case of DCBP in both polymers a significant displacement between maxima of the emission spectrum before and after irradiation is observed. This can be seen in Figure 3. The spectra presented were measured at slightly elevated pressures to avoid the relaxation processes occurring at low pressures as well as to gain emission intensity. The maximum of the spectrum of the irradiated sample is displaced to lower energy with respect to the spectrum of the nonirradiated sample. In other words one can say that the spectrum of the irradiated sample loses intensity on the high-energy side and gains on the low-energy side. This result strongly indicates that the emission spectrum of the irradiated sample is a combination of the emission from the original and from the photocreated molecules, and furthermore that the photoproduct molecules emit at lower energy than the original molecules. Moreover, it should be noticed that the change in the shape of the emission spectrum is strongly pressure and medium dependent.

3.1.2. DMABA. Continuous irradiation for about 25 min induces two major changes in the absorption spectrum of DMABA in the polymers studied. The first is a significant decrease of the absorption intensity of the main maximum located approximately at 29.8 × 10^3 cm^{-1}, at 0 kbar. The second feature is the appearance of a new absorption band extending from ≈(22.5−27.5) × 10^3 cm^{-1}. The amounts of the decrease and the growth of the absorption peaks are the largest at atmospheric pressure and decrease when pressure increases.[3] At all pressures, the light-induced changes in the absorption spectra are stable for a long time.

At atmospheric pressure, DMABA emits very weakly. However, at elevated pressures, the emission is efficient and the spectrum consists of two well-separated bands: a high-energy band (HEB), representing fluorescence, and a low-energy band (LEB), representing phosphorescence. Upon irradiation, both bands change their intensities but the character of this change depends, as for ketones, on the pressure and the type of polymeric medium. For example in PS (see Figure 4), the intensity of both the HEB and LEB increases after irradiation

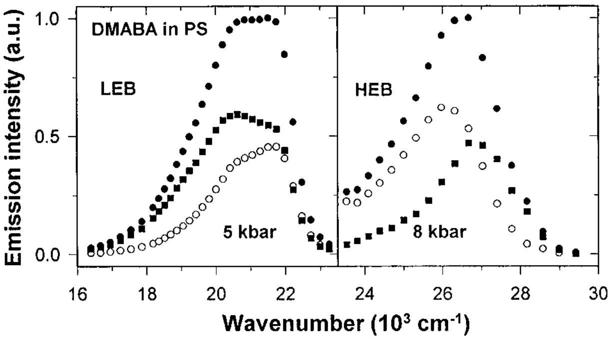

Figure 4. Emission spectra of DMABA in PS (LEB at 5 kbar and HEB at 8 kbar) before (○) and after irradiation (●) for 25 min with a flux of 7 × 10^{12} photons/s; (■) difference between before and after irradiation.

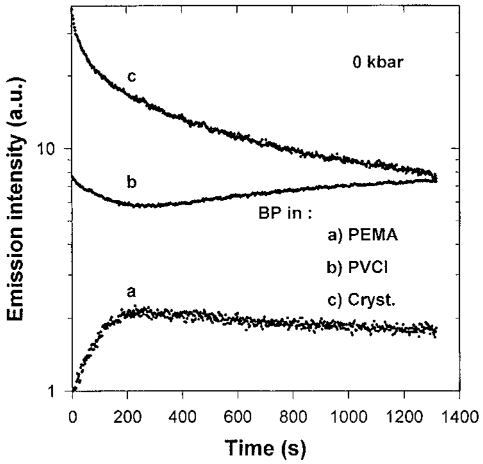

Figure 5. Phosphorescence intensity of BP at 0 kbar (at the peak maximum) under steady-state irradiation conditions in (a) PEMA, (b) PVCl, and (c) crystal.

and the resulting spectra differ from the originals. Furthermore, as one can notice, the HEB and LEB of the irradiated sample are displaced differently from the respective bands before irradiation. The HEBs and LEBs are displaced to higher and lower energy, respectively. This is clearly seen on the curve which represents a difference between the spectrum of the irradiated and nonirradiated samples (the dark squares in Figure 4). The maxima of the emission bands induced by irradiation are located approximately 1000 cm^{-1} above and 400 cm^{-1} below the original maxima of the high and low energy bands, respectively. These large differences between the original and light-induced peaks indicate strongly the different sources of the irradiated and original peaks.

3.2. Time Evolution of the Emission Intensity under Continuous Irradiation. As we have pointed in section 3.1., the change of intensity and shape of the emission spectrum upon irradiation are pressure and medium dependent. Additionally, the change of intensity is dependent on the time of irradiation. To monitor these changes, we measured, under continuous irradiation, the time evolution of the emission intensity at selected wavelengths in various environments and at different pressures. It should be pointed out that in figures where we compare irradiation effects at different pressures or involving different treatments, in each figure the initial values (at time zero) are normalized to the lowest initial value obtained for only the results presented in that figure.

3.2.1. BP and DCBP. The main features of the emission intensity at the maximum of the emission spectrum are shown at atmospheric pressure and in various environments in Figures 5 and 6 for BP and DCBP, respectively. In both crystalline

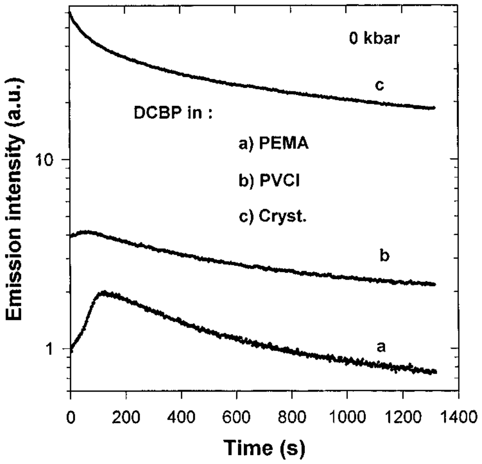

Figure 6. Phosphorescence intensity of DCBP at 0 kbar (at the peak maximum) under steady-state irradiation conditions in (a) PEMA, (b) PVCl, and (c) crystal.

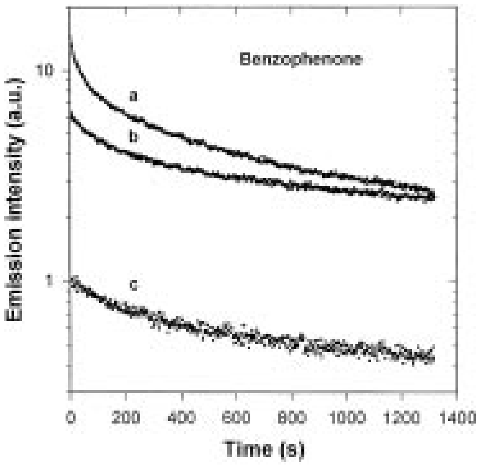

Figure 7. Phosphorescence intensity of BP crystal (455 nm line) under steady-state irradiation conditions for several pressures: (a) 0, (b) 3, and (c) 10 kbar.

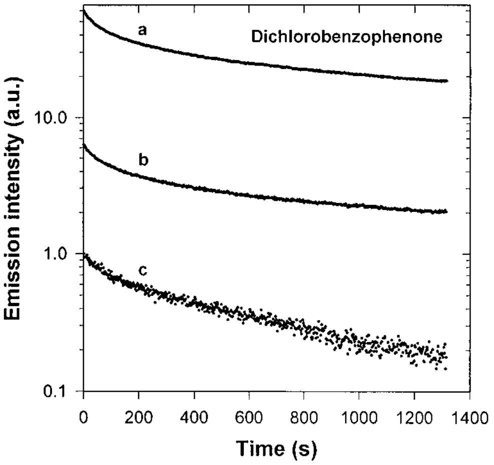

Figure 8. Phosphorescence intensity of DCBP crystal (450 nm line) under steady-state irradiation conditions for several pressures: (a) 0, (b) 3, and (c) 11 kbar.

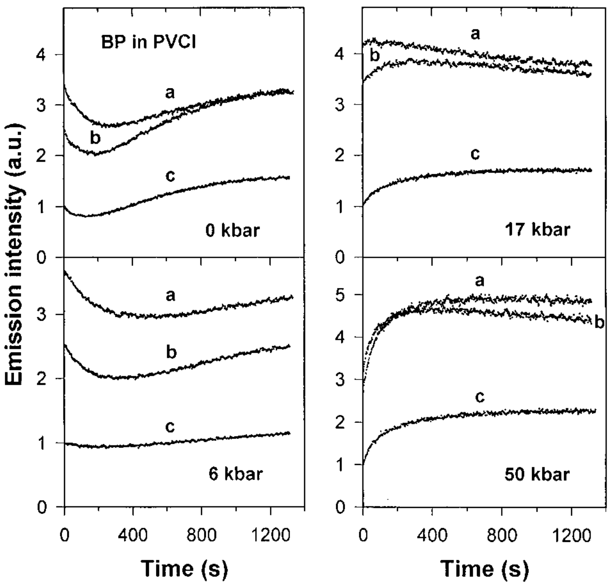

Figure 9. Phosphorescence intensity of BP in PVCl under steady-state irradiation conditions for several pressures at three emission lines: (a) 450, (b) 480, and (c) 535 nm.

samples the emission intensity decreases continuously with time of irradiation, and the same effect is observed at elevated pressures (see Figures 7 and 8 for BP and DCBP, respectively). In polymeric environments the time evolution of the phosphorescence emission is more complex than in crystals. For BP in PVCl the phosphorescence intensity initially decreases and then after longer irradiation gradually increases. However, in the remaining cases (see Figures 5 and 6), the opposite behavior is observed; there is an initial increase of intensity and then a decrease.

Under high pressure, severe changes in overall shape of the light-induced intensity curve are noticed. Furthermore, it should be clear from the previous paper that the absolute initial values are a strong function of pressure so that figures below compare the fractional changes with irradiation not the absolute magnitude of the changes. In the case of BP in PVCl (see Figure 9), the intensity curve changes its character above ≈15 kbar and then for all higher pressures consists of an initial increasing part. In contrast to the behavior in PVCl, the emission intensity of BP in PEMA shows at all pressures a gradual increase from the beginning of illumination with a tendency to saturation for longer times. Moreover, in this case, the higher the pressure, the larger the increase of the emission intensity under continuous irradiation.[2] Furthermore, in both polymers because of the strong overlap of the light-induced peak with the original peak the emission intensity curve exhibits the same characteristic features at different detection wavelengths.

DCBP, due to the observed energetic displacement of the light-induced peak with respect to the original peak, shows new features of the emission intensity curve hidden in the case of BP. In Figures 10 and 11, the curves marked a represent the intensity at the maximum of the original peak and those marked b (in PEMA) and c (in PVCl) represent the intensity on the low-energy side of the spectrum where the emission from the photoproduct occurs. If the photoproduct and original peak are well separated, the curve a would primarily reflect the change in intensity of the original molecules and curve c (or b in the case of PEMA) would primarily reflect the changes in the intensity of the photoproduct molecules. Since the above peaks are not well separated and their emission intensities may decrease or increase due to involvement of two opposing processes, a decrease of concentration of the original molecules and an increase of concentration of the photoproduct molecules, the emission intensity curves reflect the competition of these two tendencies. As one can see in Figures 10 and 11, the emission intensity is dominated by a decreasing trend at low pressures and an increasing trend at high pressures. The latter effect seems to be much stronger in the case of PEMA than that of PVCl.

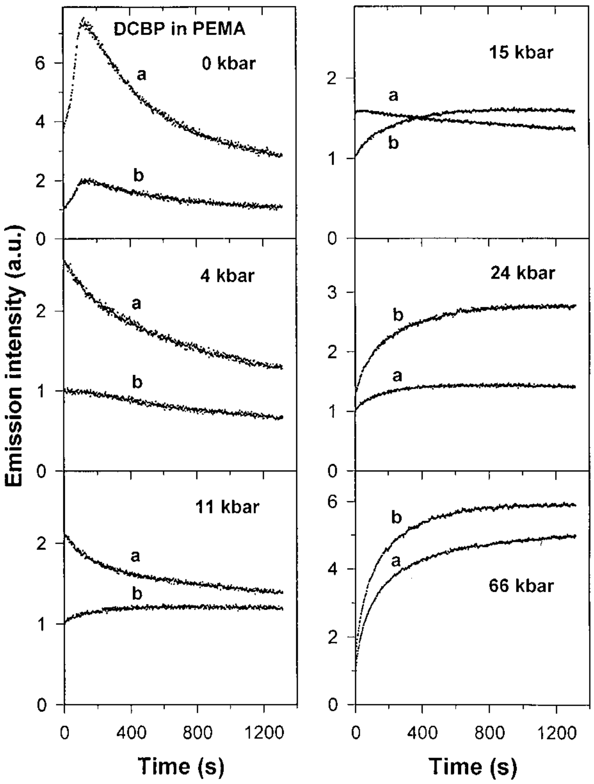

Figure 10. Phosphorescence intensity of DCBP in PEMA under steady-state irradiation conditions for several pressures at two emission lines: (a) 460 and (b) 480 nm.

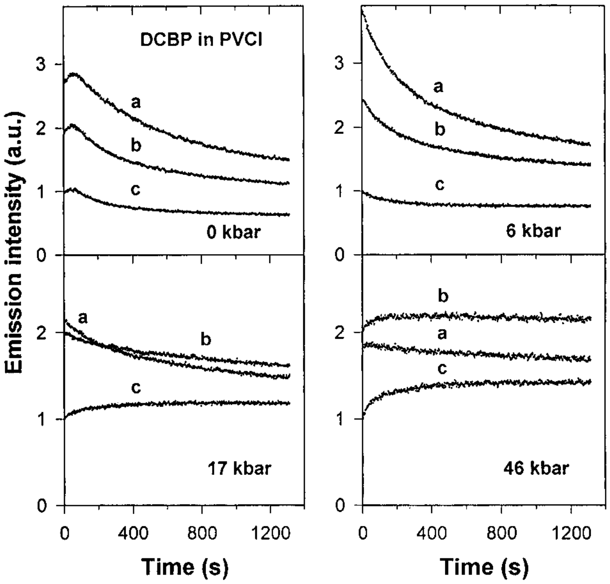

Figure 11. Phosphorescence intensity of DCBP in PVCl under steady-state irradiation conditions for several pressures at three emission lines: (a) 455, (b) 485, and (c) 535 nm.

The light-induced changes in the emission intensity are to some degree reversible at atmospheric pressure but essentially irreversible at higher pressures. At atmospheric pressure the light-induced intensity decreases when the sample is kept in the dark. In the case of DCBP in PEMA, the relaxation rate constant estimated for this process is 8.3 × 10^{-3} s^{-1}. In the second run on the same sample, the intensity can not, however, reach the maximum from the previous run. The above features are presented, for instance, in Figure 12.

If a sample is pressurized to, say, 50 kbar and after being held for an hour without irradiation, the pressure is released, subsequent irradiation shows an effect identical to that obtained for a sample which has not been pressurized.

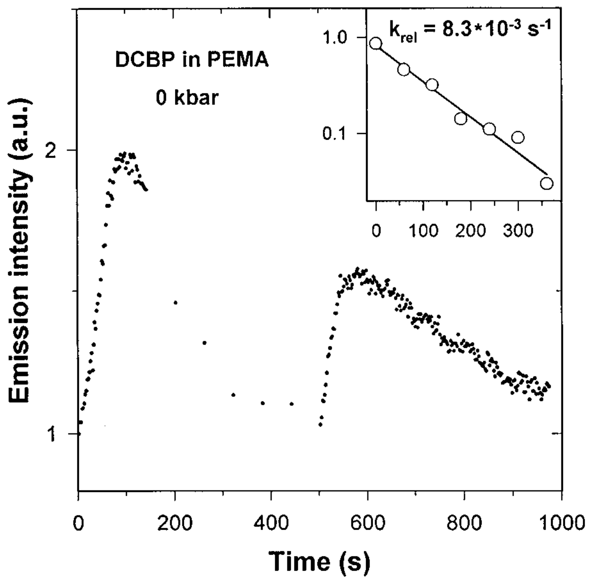

Figure 12. Change of the phosphorescence intensity of DCBP in PEMA at 0 kbar (460 nm line) under continuous and periodic irradiation conditions. After reaching the maximum value of phosphorescence, the sample was excited every minute for 2 s during which the phosphorescence was measured. From the decrease of the LIP intensity during each interval with no irradiation the relaxation constant was calculated (see inset).

If a sample is irradiated at a pressure p_1 and then taken to a pressure p_2 (which may be higher or lower than p_1) and irradiated, the time dependence of the intensity change is very similar to that of a sample taken directly to p_2 and irradiated, but the amount of the effect is significantly smaller.

The behavior of DMABA (discussed below) under the conditions described in the above two paragraphs is very similar to that of BP and DCBP.

3.2.2. DMABA. The emission intensity of the LEB and HEB of DMABA, in all three matrices studied, changes drastically upon irradiation (see Figures 13−15). At low pressures, the LEB intensity, initially extremely low and being assigned to the phosphorescence emission, increases enormously during continuous irradiation. At atmospheric pressure, a typical curve of the phosphorescence intensity versus irradiation time (curve a in the lower part of Figures 13−15) consists of three characteristic regions: (1) a period during which the phosphorescence intensity, is almost unchanged, (2) a fast and large increase of the phosphorescence intensity and (3) a gradual but marked decrease of the intensity at longer irradiation times. The relative significance of these three regions changes in each polymer. For instance, in PVCl the phosphorescence intensity increases just at the beginning of irradiation, showing no initial period. With increase of pressure the time evolution of the phosphorescence intensity shows new features. The initial period practically disappears and the fraction of the intensity increase decreases as pressure increases. Finally, above a certain pressure the emission intensity does not increase but only decreases. The switch from the increasing tendency of the emission intensity curve to the decreasing tendency takes place at different pressures for various polymers but lowest in PVCl. In this case even at 5 kbar there is only a decrease of phosphorescence intensity.

The increase of the phosphorescence intensity at 0 kbar has no permanent character. As can be seen in Figure 16 (upper part) the phosphorescence intensity decreases during each

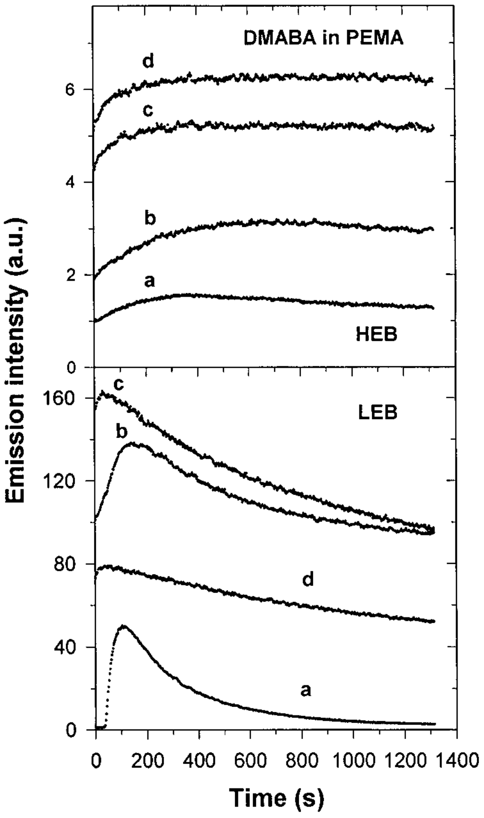

Figure 13. Luminescence intensity of DMABA in PEMA under steady-state irradiation conditions at different pressures. LEB: (a) 0, (b) 7, (c) 11, and (d) 50 kbar. HEB: (a) 0, (b) 6, (c) 24, and (d) 60 kbar.

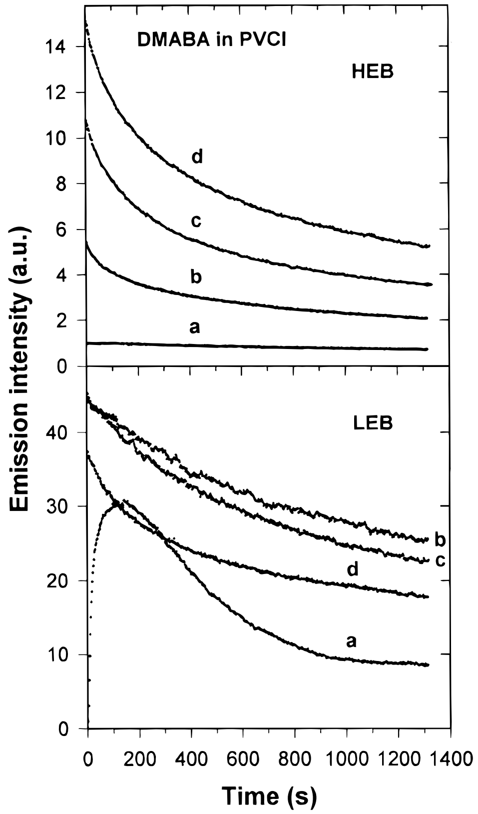

Figure 14. Luminescence intensity of DMABA in PVCl under steady-state irradiation conditions at different pressures. LEB: (a) 0, (b) 5, (c) 11, and (d) 57 kbar. HEB: (a) 0, (b) 10, (c) 32, and (d) 70 kbar.

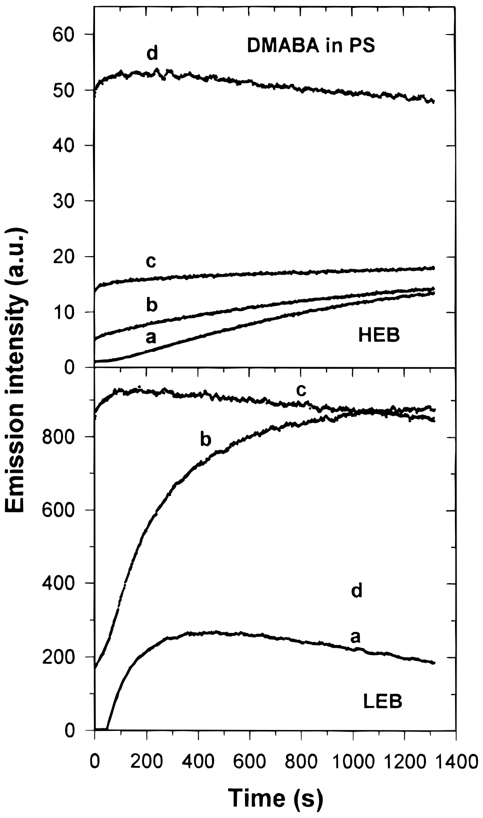

Figure 15. Luminescence intensity of DMABA in PS under steady-state irradiation conditions at different pressures. LEB: (a) 0, (b) 5, (c) 15, and (d) 36 kbar. HEB: (a) 0, (b) 10, (c) 30, and (d) 57 kbar.

interval when sample is kept in the dark (no irradiation). The rates of reduction of the light-induced phosphorescence intensity in the dark were estimated to be 4×10^{-2}, 2.5×10^{-2}, and 3.5×10^{-3} s^{-1}, respectively in PEMA, PS, and PVCl. These rates are 2 orders of magnitude lower than the emission rate constants of the triplet state (e.g. 6 s^{-1} in PEMA, at 0 kbar). Although the light-induced phosphorescence intensity decreases in the dark in a few minutes, in the second run on the same sample the maximum emission intensity is lower than the final value from the previous run. This indicates the presence of some irreversible processes even at atmospheric pressure. In the sample under pressure, unlike at atmospheric pressure, the light-induced phosphorescence intensity is very stable in time when the sample is kept in the dark. This pressure stabilization of the irradiation-induced effect takes place regardless of the character of the light-induced changes, increase or decrease, pointing out the highly irreversible nature of the processes.

The time evolution of the fluorescence intensity (HEB) during continuous irradiation reveals some different features from the phosphorescence curves (LEB). Firstly, as one sees in Figures 13−15 (upper part), the changes in the fluorescence intensity are much smaller than for the phosphorescence intensity. Secondly, the light-induced changes in the fluorescence intensity appear at the beginning of irradiation; the intensity curve has no initial, dead period. Thirdly, the change of pressure does not affect the shape of the light-induced curve as much as it does in the case of phosphorescence. In PEMA and PS at all pressures there is essentially only an increase of fluorescence intensity but in PVCl, in contrast, only a decrease. Furthermore, as can be seen in Figure 16 (lower part), the decrease of the light-induced fluorescence intensity in the dark is almost 2 orders of magnitude lower than in the case of phosphorescence. Thus, the light-created fluorescent entities seem to be much more stable than phosphorescent entities.

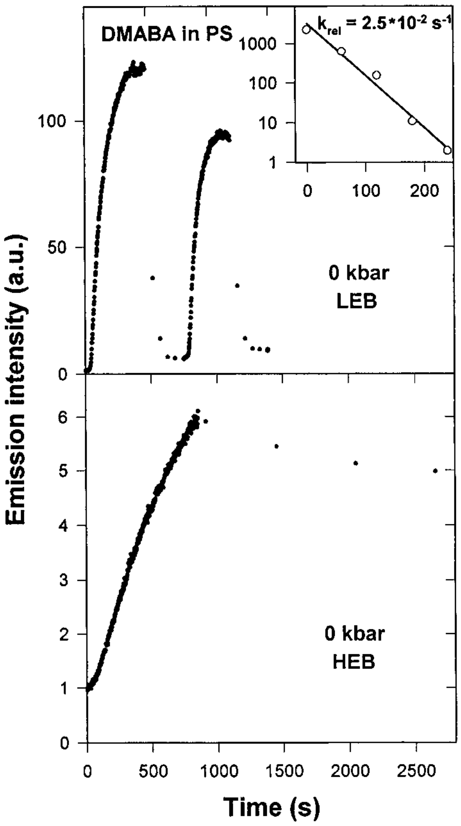

Figure 16. Emission intensity of DMABA in PS (LEB and HEB) at 0 kbar under steady-state conditions (rising parts of curve). For the descending part of the curves the sample was excited for 2 s every minute (LEB) and every 10 min (HEB). The inset includes the rate of relaxation taken from the descending part of the first cycle of the LIP curve.

4. Discussion

As is evident from the Results section above, we have developed an extensive number of comparisons of the pressure and previous sample treatment on the luminescent properties of these compounds under continuous irradiation in various media. In this section we discuss in detail those effects for which we can present a reasonable model or soundly based set of arguments. It is hoped that the other results will form the basis for future experimentation and analysis.

The curves representing a time evolution of the emission intensity under continuous irradiation show complex features. Nevertheless, in general, one can distinguish two clear competing trends: an increase and/or decrease of the emission intensity. As we have pointed before these trends can be a result of the creation of emissive and nonemissive species due to a high photoreactivity of the triplet state. The relative importance of these two processes is strongly medium and pressure dependent. The most characteristic feature of these dependencies is the fact that in crystalline samples the emission intensity at all pressures decreases and this decrease is irreversible. This indicates that in the crystals there is only present a process which transforms the molecules permanently into nonemissive species. Since in the crystal molecules are fixed in mutual configuration which is not favorable for the bimolecular reactions and, in addition, the hydrogens attached to the benzene ring are essentially resistant against abstraction, the hydrogen abstraction reaction can be ruled out as a driving force for the intensity change in crystalline BP and DCBP. In this case, two processes that reduce the number of active molecules can be considered: an ionization of molecule due to two-photon triplet absorption and/or a bond cleavage. The decrease of the emission intensity shows a strong excitation intensity dependence;[2,3] thus, we believe that a two-photon process is primarily responsible for removing molecules from the irradiated system. Since we cannot determine this process in detail, the double-excited triplet state can essentially be a precursor either to the ionization or cleavage process.

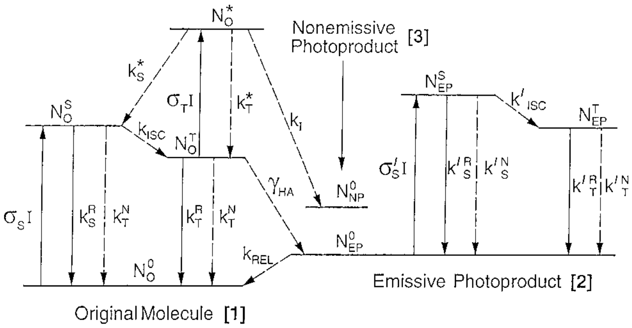

Figure 17. Scheme of the kinetic model. The meaning of the symbols can be found in the text.

In the polymeric media, in addition to the destructive process describe above, a process responsible for the creation of an emissive species takes place and in many cases this process predominates. Since this kind of photoreactivity requires the presence of the polymer, we believe that the process has a source in the hydrogen abstraction reaction. Furthermore, a different dependence on the incident light intensity of the increasing part than of the decreasing part of the emission curve indicates that this reaction may not take place from the same higher excited state as the ionization process. Although the exact process of the hydrogen reaction could not be determined, we postulate that this process may be primarily connected with the lowest triplet state. It should be noted that in the polymer matrix, where diffusion of solute is highly restricted, interaction between solute and solvent is limited to the closest surroundings. Therefore, the cage and geminate effects are proposed to play an important role in the hydrogen abstraction process in solid media.[19,26] On the first stage of this process a cage-radical pair is assumed to be formed. Then, this geminate pair of molecular and macromolecular radicals may undergo recombination or disproportionation. In the former case an original molecule is reproduced. The disproportionation is understood to involve a short distance of separation, supposedly due to reorientation of the two fragments of the geminate pair with respect to each other. Ultimately, a stable photoproduct (at atmospheric pressure the stability of the photoproduct is limited to several minutes) can be formed. In the systems studied, the exact form (nature) of the final, emissive photoproduct cannot be determined. However, it is believed that it could be a some kind of adduct between polymer and solute molecule.

4.1. The Kinetic Model. The scheme of the kinetic model proposed, with relevant levels and rate parameters, is presented in Figure 17 and can be used, as we show, to give a first-order description for a reasonable fraction of results. The phenomena of interest originate from the triplet state of the molecule. There are three possible paths from this state: (**1**) spontaneous deactivation consisting of phosphorescence and nonradiative deactivation process, (**2**) reaction with the polymer by abstracting a hydrogen atom from the polymer and ultimately forming an emissive photoproduct, and (**3**) excitation to the higher excited state (a two-photon process) and creation of a nonemissive photoproduct. For the molecules studied, process **1** has a rate constant ($k_T = k_T{}^R + k_T{}^N$) at room temperature in the range $10^2-10^4\ s^{-1}$ that is several orders of magnitude lower than the rate for the singlet state ($k_S = k_S{}^R + k_S{}^N$). In process **2** the emissive photoproduct created with a time dependent rate (γ_{HA})

then absorbs the exciting light giving an emission spectrum which may or may not differ significantly in energy from that of the original molecule. The emissive photoproduct in some cases at or near atmospheric pressure may undergo a reversible reaction in the ground state with a rate constant $k_{\rm REL}$ (a relaxation process) reproducing the original molecule. In our opinion, in spite of the relatively low excitation flux, the long lifetime of the triplet state makes process **3** feasible. In this process a doubly excited molecule can decay back to the excited singlet (k_S*) or triplet (k_T*) or can react irreversibly (k_I) to form an ion or other entity which is trapped indefinitely. This latter process removes a molecule from the system permanently.

The processes listed above are described by the following set of equations:

$$dN_O{}^S/dt = \sigma_S I N_O{}^0 - (k_S + k_{ISC})N_O{}^S + k_S{}^*N_O{}^* \qquad (1)$$

$$dN_O{}^T/dt = k_{ISC}N_O{}^S - (k_T + \sigma_T I + \gamma_{HA})N_O{}^T + k_T{}^*N_O{}^* \qquad (2)$$

$$dN_{EP}{}^0/dt = \gamma_{HA}N_O{}^T - (\sigma_S{}'I + k_{REL})N_{EP}{}^0 + k_S{}'N_{EP}{}^S + k_T{}'N_{EP}{}^T \qquad (3)$$

$$dN_{EP}{}^S/dt = \sigma_S{}'IN_{EP}{}^0 - (k_S{}' + k_{ISC}{}')N_{EP}{}^S \qquad (4)$$

$$dN_{EP}{}^T/dt = k_{ISC}{}'N_{EP}{}^S - k_T{}'N_{EP}{}^T \qquad (5)$$

$$dN_O{}^*/dt = \sigma_T I N_O{}^T - (k_I + k_S{}^* + k_T{}^*N_O{}^* \qquad (6)$$

$$dN_{NP}{}^0/dt = k_I N_O{}^* \qquad (7)$$

In the above equations I stands for the intensity of the excitation light. σ_S and σ_S' are the singlet ground-state absorption cross sections, respectively, for the original molecule and for the emissive photoproduct, and σ_T is the absorption cross section of the excited triplet state of the original molecule. $N_O{}^0$, $N_O{}^S$, $N_O{}^T$, and N_O* are the concentrations of the original molecules in the ground, singlet, triplet, and higher excited states, respectively. $N_{EP}{}^0$, $N_{EP}{}^S$, $N_{EP}{}^T$ are the concentrations of the emissive photoproduct in the ground, singlet, and triplet states, respectively. $N_{NP}{}^0$ is the concentration of the nonemissive photoproduct in the ground state. The remaining k and k' symbols correspond, respectively, to the original molecule and emissive photoproduct and have their commonly used meanings.

Where all three processes are occurring simultaneously and in significant degree, the analysis involves too many variables to be handled, but there are circumstances where processes **1** and **2** or processes **1** and **3** are dominant. We present below analyses for these two cases and apply them especially to the ketones where the properties of the medium and/or the pressure allows the appropriate simplification.

(I) In the case when only pathways **1** and **2** are present (the hydrogen abstraction process predominates), since the singlet and also triplet state equilibrate much faster than the concentration of the emissive photoproduct, steady-state conditions can be applied to eqs 1, 2 and 3, 4. Then eqs 1−5 can be rewritten in the following form:

$$\sigma_S I[N_O{}^0(0) - N_{EP}{}^0] - (k_S + k_{ISC})N_O{}^S = 0 \qquad (8)$$

$$k_{ISC}N_O{}^S - k_T N_O{}^T = 0 \qquad (9)$$

$$dN_{EP}{}^0/dt = k_{HA}[N_{PL}(0) - N_{EP}{}^0]N_O{}^T \qquad (10)$$

$$\sigma_S{}'IN_{EP}{}^0 - (k_S{}' + k_{ISC}{}')N_{EP}{}^S = 0 \qquad (11)$$

$$k_{ISC}{}'N_{EP}{}^S - k_T{}'N_{EP}{}^T = 0 \qquad (12)$$

In these equations $N_O{}^0(0)$ and $N_{PL}(0)$ stand, respectively, for the initial, at time zero, concentration of the original molecules and the sites available for hydrogen abstraction sites in the polymer. k_{HA} is the bimolecular rate coefficient for the overall hydrogen abstraction reaction (primary and secondary processes), related to γ_{HA} by the following relation: $\gamma_{HA} = k_{HA}N_{PL}$ (N_{PL} is the time dependent concentration of the sites in the polymer available for hydrogen abstraction).

The time dependence of the phosphorescence intensity from the emissive photoproduct can be defined as follows

$$I_{EP}(t) = k_T{}'^R N_{EP}{}^T(t) \quad \text{or} \quad I_{EP}(t) = AN_{EP}{}^0(t) \qquad (13)$$

where

$$A = (k_T{}'^R/k_T{}')[\sigma_S{}'I/(1 + k_S{}'/k_{ISC}{}')] \qquad (14)$$

The above function can be found but in a nonexplicit form by solving eqs 8−12

$$Bt = \{k_T + k_{HA}[N_{PL}(0) - N_O{}^0(0)]\} \log[1 - I_{EP}(t)/(AN_O{}^0(0))] - k_T \log[1 - I_{EP}(t)/(AN_{PL}(0))] \qquad (15)$$

with

$$B = \sigma_S I/(1 + k_S/k_{ISC}) \qquad (16)$$

(II) In the case when only pathways **1** and **3** are present (a two-photon process predominates), the time dependence of the phosphorescence intensity from the original molecules can be obtained by solving the following set of equations:

$$\sigma_S I N_O{}^0 - (k_S + k_{ISC})N_O{}^S = 0 \qquad (17)$$

$$k_{ISC}N_O{}^S - (k_T + \sigma_T I)N_O{}^T = 0 \qquad (18)$$

$$dN_O{}^*/dt = \sigma_T I N_O{}^T - k_I N_O{}^* \qquad (19)$$

$$dN_O{}^0/dt = - k_I N_O{}^* \qquad (20)$$

It should be noted that in eq 19 the backward processes from the higher excited state to the singlet and triplet states are, in the first approximation, assumed to be negligible. With these assumptions one obtains an expression for relative change of the phosphorescence intensity, at time t, under continuous irradiation in the following form

$$I_{PH}(t)/I_{PH}(0) = (a_2 - a_1)^{-1}\{(a_2 - c)\exp(-a_1 t) - (a_1 - c)\exp(-a_2 t)\} \qquad (21)$$

where

$$a_{2,1} = \{k_I \pm (\,k_I{}^2 - 4k_I D)^{1/2}\}/2, \quad c = (k_I N_O{}^*(0))/N_O{}^0(0) \qquad (22)$$

$$D = (\sigma_S I)/(1 + k_T/\sigma_T I)(1 + k_S/k_{ISC}) \qquad (23)$$

N_O*(0) is the concentration of the original molecules in the higher excited state at the time of the first act of excitation (we denote this time as zero).

Equations 15 and 21 obtained for the two limiting cases will be used for comparison of the model predictions with the particular results that may be consistent with these cases. In the case when all three **1**−**3** processes are present and are comparable in size, one can at least expect that the analytical solution should be a combination of eqs 15 and 21. Since the combined equation would have even more unknown parameters than either eq 15 or 21, we focus only on these two isolated cases.

4.2. Comparison of Results with the Model. *4.2.1. BP and DCBP.* As has been mentioned above the processes that govern the irradiation effect in BP and DCBP crystals may be best described by case II, i.e. with the absence of the hydrogen abstraction reaction. Assuming the validity of the model, the experimental results for the phosphorescence emission change can be then compared with eq 21. The fit of this equation to some typical results is shown in Figure 18. As can be seen, the analytical expression 21 for certain sets of a_1, a_2 and c parameters gives a very good fit to the experimental curves. Since these parameters are coupled with the physical parameters, one can obtain additional information on the latter from the following relations:

$$k_I = a_1 + a_2 \tag{24}$$

$$N_O^*(0)/N_O^0(0) = c/(a_1 + a_2) \tag{25}$$

$$D = (a_1 + a_2)\{1 - [(a_1 - a_2)/(a_1 + a_2)]^2\}/4 \tag{26}$$

The above quantities for BP and DCBP crystals are compared in Table 1 for several pressures. Although the results cover a limited pressure range (above ~15 kbar the emission intensity was almost undetectable), some conclusions about pressure dependencies can be made. First of all, as one sees in Table 1, all three parameters for either BP or DCBP decrease with increasing pressure but in larger degree for BP than DCBP. For example, the rate constant for the irreversible reaction (k_I) decreases in the case of BP almost four times but hardly changes for DCBP. Since the process denoted by the rate k_I consists basically of two steps, an ionization of the molecule and then separation of the ionized fragments, it is not clear, from our results, how each of these steps participate in the pressure dependence of k_I. However, if one notices that the energy of the triplet state hardly changes with pressure (at least in the range of interest, i.e. over the first 10 kbar) then the first step of ionization, which is primary energetically determined, should not be pressure dependent. On the other hand, it is conceivable to assume that with increasing pressure the probability for separation of ionized fragments might decrease due to the reduction of the available intermolecular space.

The ratio of the initial occupation of the higher excited state to the population of molecules in the ground state decreases slightly with pressure, but it does not seem to be a meaningful effect. Essentially, one can say that the values of $N_O^*(0)/N_O^0(0)$, regardless of the pressure and the type of material, assume the same average (0.4) value.

Since, for BP and DCBP, $k_{ISC} \gg k_S$, the factor D assumes form of $(\sigma_S I)/(1 + k_T/(\sigma_T I))$. At the same experimental conditions and with unchanged absorption coefficient, the value of D is proportional to $(1 + (k_T^R + k_T^N)/(\sigma_T I))^{-1}$. Thus, the observed decrease of D with pressure would indicate an increase of k_T. Furthermore, as results from the preceding paper show, this increase of k_T in BP and DCBP crystals can be caused by pressure enhancement of the nonradiative rate (k_T^N) from the lowest triplet state.

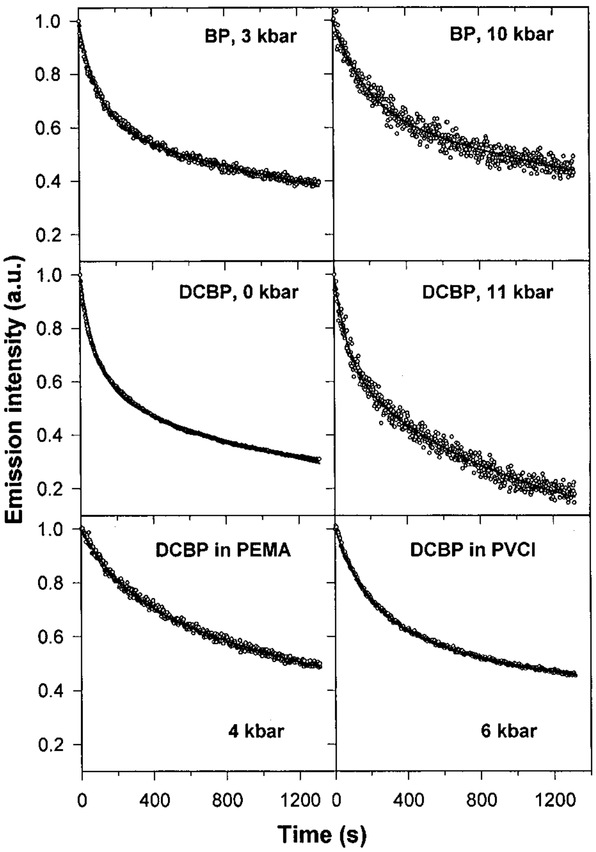

Figure 18. Fit of eq 21 to some typical experimental results where the emission intensity curve obtained under continuous irradiation reveals a decrease with time. The original results are presented in Figures 7, 8, 10, and 11, respectively for BP, DCBP, and DCBP in PEMA and PVCl. The parameters assuring the best fit in each case are presented in Table 1.

TABLE 1: Parameters of the Best Fit of Eq 21 to Experimental Results Obtained for BP and DCBP Crystals and DCBP in PEMA and PVCl

p (kbar)	k_I (s^{-1})	$N_O^*(0)/N_O^0(0)$	D
	BP Crystal		
0	2.0×10^{-2}	4.6×10^{-1}	7.0×10^{-4}
3	9.6×10^{-3}	3.9×10^{-1}	3.5×10^{-4}
10	5.5×10^{-3}	3.6×10^{-1}	2.8×10^{-4}
	DCBP Crystal		
0	1.4×10^{-2}	4.4×10^{-1}	9.4×10^{-4}
3	1.2×10^{-2}	4.3×10^{-1}	5.0×10^{-4}
11	1.1×10^{-2}	3.6×10^{-1}	4.5×10^{-4}
	DCBP in PEMA		
4	5.0×10^{-3}	3.9×10^{-1}	2.3×10^{-4}
	DCBP in PVCl		
6	4.5×10^{-3}	2.8×10^{-1}	3.1×10^{-4}

Although in the polymeric media the intensity change curves exhibit, in general, complex features, indicating a competition of all three **1**−**3** processes, one finds two examples where only a decrease is observed. These are DCBP in PEMA and PVCl, respectively, at 4 and 6 kbar. We believe that in these cases processes **1** and **3** predominate (case II), and it seems to be informative to apply the eq 21 to fit these results. The accuracy of the fit is shown in Figure 18, and the fitting parameters are shown in the Table 1. On the basis of these two examples, it is difficult to draw a general conclusion on the character and pressure dependence of the ionization effect in the polymeric matrices. Nevertheless, it is seen that k_I is noticeably smaller

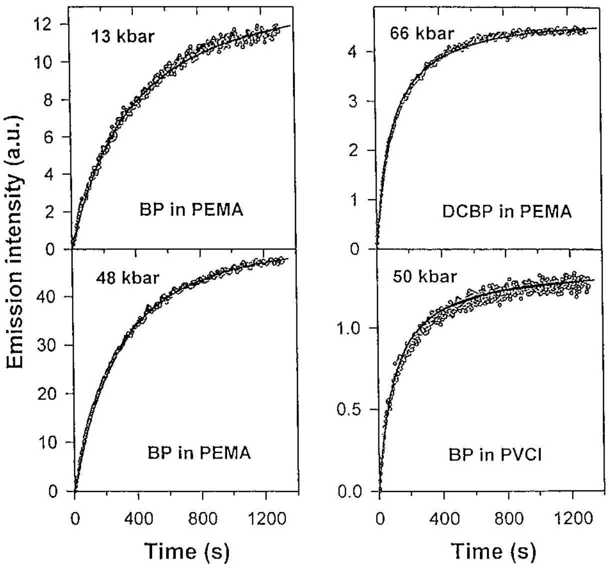

Figure 19. Fit of the eq 15 to some experimental results where an increase of the emission intensity with time is recorded. The parameters of the best fit in each case are listed in Table 2.

in the polymers than in the crystal. Since k_{I} stands for both the formation and separation of the ionized pairs, the smaller value of k_{I} in the polymer could simply indicate a lower efficiency of the ionization process in the polymeric medium. One of the factors responsible for this could be a higher ionization potential in the polymer than in the crystal. It is well-known that the ionization potential of a given molecule in a condensed phase is lowered by an amount equal to the polarization energy with respect to the ionization potential for the isolated molecule. The polarization energy is usually smaller in polymers than in the crystal,[27] so the energy required for the ionization of the same molecule in the polymer would be higher than in the crystal. In our experiments, the energy provided to the molecule in any media is the same;[28] thus, in the crystalline environment the molecule is able to attain the states of higher energy in the ionization continuum than in the polymer. It seems to us that this could be the reason for the relatively lower ionization efficiency in the polymer as compared to the crystal.

The cases when the emission intensity only increases during continuous irradiation can be approximately described by eq 15. In Figure 19 there are shown a few examples of fitting eq 15 to some experimental curves when an increase of the intensity is unquestionable. These are the results for BP in PEMA at several pressures, taken from a previous paper,[2] and also BP in PVCl and DCBP in PEMA only at the highest pressure. In the fitting procedure, in order to reduce the number of unknown parameters, the value of $N_{\mathrm{O}}^0(0)$ was fixed. Although this value was taken somewhat arbitrarily, we have determined that the knowledge of the exact value of $N_{\mathrm{O}}^0(0)$ is not crucial to assure either a correctness of the pressure dependence of the remaining parameters or a high quality of the fit. If a different $N_{\mathrm{O}}^0(0)$ is taken, the values of $N_{\mathrm{PL}}(0)$, k_{HA}, and A change relative to $N_{\mathrm{O}}^0(0)$, maintaining, however, the same pressure dependence and the same excellent fit. Since we focus on the pressure dependencies of the fitting parameters, their absolute values are much less important in this consideration. The parameters of the best fit, with $N_{\mathrm{O}}^0(0) = 10^{10}$, are collected in Table 2. On the basis of the case of BP in PEMA, we are able to examine the effect of pressure on some parameters involved in the model. As can be seen, two of these parameters, k_{HA} and A, show a clear trend of change when pressure increases. Over the range of 40 kbar, the k_{HA} rate decreases almost 2.5 times and the parameter A increases more than 1 order of magnitude. Since the k_{HA} rate represents a process consisting of three steps, (i) an abstraction of the hydrogen atom by the carbonyl molecule from the polymer and formation of two radicals, (ii) a separation of the radicals in the geminate cage, and (iii) a secondary reaction of the radicals producing an emissive photoproduct, the pressure increase may contribute to changes at all these stages. It seems, however, that a decrease of k_{HA} under increasing pressure can be essentially caused by two factors: a decrease of the triplet state reactivity due to an increase of its π,π^* character and a decrease of the separation efficiency of the hydrogen abstraction-created radicals in the compressed environment.

So far, we have discussed the effect of the emission intensity increase for BP in PEMA. In this case the effect is the largest among the systems studied, and, in contrast to the other cases, it is detected even at pressures near 1 atm. In the remaining cases the continuous increase of the emission intensity was observed only at highest pressures. As can be noticed from the Table 2, in these cases the k_{HA} rate is much smaller than for BP in PEMA. On the basis of this result one can say that the hydrogen abstraction reaction proceeds with a significantly smaller rate for DCBP than for BP and also with a smaller rate in PVCl than in PEMA. Thus the systems studied could be arranged in the following order of decreasing value of the k_{HA} rate: (BP in PEMA) > (DCBP in PEMA) > (BP in PVCl) > (DCBP in PVCl).

As has been mentioned above, the parameter A shows a distinct pressure trend. It can be seen that under the same experimental conditions the parameter A is proportional to $(1 + k_{\mathrm{T}}'^{\mathrm{N}}/k_{\mathrm{T}}'^{\mathrm{R}})^{-1}$; thus, its increase with pressure would indicate a change of the radiative or/and nonradiative rate of the triplet state of the emissive photoproduct. It is highly probable that as pressure increases the triplet state of the emissive photoproduct enhances its π,π^* character. This in turn results in the increase of the $k_{\mathrm{T}}'^{\mathrm{R}}$ rate.

The comparison of results with the model, presented above, concerned the simple cases when the hydrogen abstraction or ionization prevails. However, most of the data show a competition between both effects. The relative importance of these two effects can be strongly perturbed by pressure. Below we discuss briefly some of these results. At low pressures, BP and DCBP in the polymeric matrices exhibit a complex behavior for the emission intensity curves induced by continuous irradiation. In these cases, the emission intensity increases as well as decreases. However, as the pressure gets higher one observes an increase in the tendency for the emission to increase rather than decrease with time. There are three conceivable reasons for this effect: (i) an increase in rate of hydrogen abstraction and formation of the emissive photoproduct, (ii) an increase in the luminescence efficiency of the emissive photoproduct and (iii) a decrease in the efficiency of the formation of the nonemissive entity. The first of these can be eliminated because the increasing π,π^* nature of the original triplet state with pressure surely decreases the efficiency of hydrogen abstraction. The second cause is highly likely as there is an excellent probability that the π,π^* content of the triplet state of the photoproduct molecule increases with pressure. As discussed previously[2,4] pressure tends to stabilize π,π^* states relative to n,π^*, and π,π^* emissions are, in general, much more efficient than n,π^*. The third factor is more problematical, especially since the nature of the nonemissive photoproduct cannot be definitely established. With increased compression one can conceive of increased geometrical limitations on the formation of the nonemissive photoproduct.

The irradiation-induced emission characteristics for ketones are distinctly medium dependent. In the crystal one observes

TABLE 2: Parameters of the Best Fit of Eq 15 to the Curves of the Some Experimental Results

	pressure (kbar)					
	BP in PEMA				BP in PVCl	DCBP in PEMA
parameters	5	13	30	48	50	66
B	2.2×10^{-1}	4.0×10^{-1}	2.7×10^{-1}	3.9×10^{-1}	2.0×10^{-1}	2.0×10^{-1}
k_T	2.0×10^{3}	1.8×10^{3}	2.2×10^{3}	1.5×10^{3}	8.0×10^{2}	9.0×10^{2}
k_{HA}	4.4×10^{-7}	2.7×10^{-7}	3.0×10^{-7}	1.6×10^{-7}	2.7×10^{-9}	4.3×10^{-9}
$N_{PL}(0)$	9.5×10^{9}	9.0×10^{9}	9.6×10^{9}	9.1×10^{9}	9.5×10^{9}	9.5×10^{9}
$N_O^0(0)$	1.0×10^{10}	1.0×10^{10}	1.0×10^{10}	1.0×10^{10}	1.0×10^{10}	1.0×10^{10}
A	4.0×10^{-10}	1.5×10^{-9}	3.5×10^{-9}	5.8×10^{-9}	5.0×10^{-10}	1.4×10^{-10}

only process **3**, the irreversible reaction to the nonemissive photoproduct. This is expected as the hydrogen abstraction process does not occur. There is also a clear difference between the relative importance of processes **2** (hydrogen abstraction) and **3** in PVCl and PEMA. Relatively speaking process **2** is less effective in PVCl probably because in this more polarizable medium the π,π^* content of the triplet state is higher from the beginning so that hydrogen abstraction is less effective. It should be noted that for DCBP process **3** is somewhat more important than for BP, indicating higher irreversible reactivity for the dichloro derivative than for unsubstituted BP. Since process **3** proceeds very similarly for DCBP and BP in their crystalline environment, the difference in the polymers could have an intermolecular origin.

4.2.2. DMABA. The phosphorescence emission of DMABA in the polymeric media shows distinctly different behavior with increasing pressure than for BP and DCBP. Since in the latter cases the pressure enhances the tendency to increase the light-induced phosphorescence intensity during continuous irradiation, in the former case the pressure reduces this tendency. Thus, at higher pressure the intensity decreases rather than increases. This pressure effect can be explained if one assumes that the lowest triplet of the emissive photoproduct, in contrast to the original molecule, has primarily π,π^* character assuring its high emission efficiency. Thus, at 1 atm the light-induced phosphorescence intensity increases significantly with time of irradiation, but with increasing pressure due to a reduction of the overall hydrogen abstraction process (k_{HA}), the irreversible process **3** in the original molecules predominates, resulting in a strong influence of the decreasing tendency on a time dependent phosphorescence curve.

Since the original molecule of DMABA exhibits phosphorescence as well as fluorescence, continuous irradiation is expected to influence both emissions, and the effect of this influence is expected to be qualitatively similar in both cases. Surprisingly, the light-induced fluorescence curves reveal some different features with respect to the phosphorescence curves. Some of these dissimilarities are (i) at atmospheric pressure, a negligible decrease of the light-induced fluorescence intensity in the dark (without irradiation), in contrast to an essentially total decrease of the light-induced phosphorescence intensity, within a few minutes (Figure 16), (ii) at higher pressure, an increase of the light-induced fluorescence intensity but only a decrease of the light-induced phosphorescence (Figures 13, 15), and (iii) an absence of the induction period for the light-induced fluorescence curve. On the basis of these observations, it is hard to conceive that the light-induced fluorescence and phosphorescence come from the same source. A satisfactory explanation can be given if one assumes creation of two sets of emissive photoproducts of which one is essentially fluorescent and another phosphorescent. This assumption would account for different relaxation times for the phosphorescent and fluorescent species in the ground state and for different time dependence of the induced emissions under continuous irradiation. It seems that the fluorescent and phosphorescent photoproducts could be represented by two different conformers of the same emissive photoproduct, differing presumably in the mutual orientation of the carbonyl and dimethylamino groups.[29] These two ground state conformers might be responsible for the observed differences between the light-induced fluorescence and the light-induced phosphorescence. Applying this concept, an outline of the pressure dependence of the light-induced emissions of DMABA can be drawn as follows: the increase of pressure will primarily decrease the efficiency of process **2** and also change the ground state occupation of the emissive photoproduct, favoring an increase of the fluorescent species rather than the phosphorescent one. Thus, at high pressure the light-induced fluorescence curves still show an increase of the intensity during continuous irradiation, but the phosphorescence curves show only a decrease. In the latter case, path **3** seems to be the dominant process.

For DMABA there were no cases in which pathways **1** and **2** or **1** and **3** were predominant. There were a few pressures where only a decrease of emission intensity was observed (DMABA in PVCl), either for fluorescence or phosphorescence. These gave fits to eq 21 comparable in precision to those shown for BP and DCBP in Figure 18, and the same order of magnitude for the relevant parameters, but there were not sufficient pressures where eq 21 could be applied to permit rigorous identification of any trends.

5. Conclusions

We have presented results of the continuous laser irradiation on the emission intensity of BP, DCBP, and DMABA in crystalline and polymeric environments. The picture that emerges from this study is that continuous irradiation causes significant changes in the emission spectra and intensity of these compounds, and these changes are strongly pressure and media dependent. These light-induced changes are interpreted in terms of the photoinduced production of the emissive and nonemissive species that bring about changes in the ground state concentration of the molecules. These processes originate in the triplet state that has both a long lifetime and essentially an n,π^* character. Two competing processes are proposed to account for the increase and decrease of the emission intensity: an abstraction of the hydrogen atom from the polymer by the triplet state of the original molecule and ionization of these molecules due to the photon absorption by the excited triplet state. The relative importance of these two processes is strongly medium and pressure dependent. For example, in BP and DCBP crystals, only ionization participates in the intensity change while at the highest pressures in the polymers there is no sign of this process. Thus the photoreactivity of these molecules can be controlled by changing of the pressure and/or type of medium. The pressure effect on the light-induced emission intensity increase is interpreted as involving changes in the relative amounts of π,π^* and n,π^* character of the triplet state of both the original molecule and emissive photoproduct. The first process is expected to decrease the formation of the emissive photoproducts due to either a lower reactivity of the triplet state (a decrease of the n,π^* character) or hindrance of the separation of the radicals. The second process, a modification of the character of the emissive photoproduct triplet state, could either increase or decrease the light-induced emission, depending on the initial character of this triplet. A combination of the above processes and the irreversible ionization gives the final pressure dependence of the light-induced emission. The kinetic model taking into account these processes is developed and solved for two cases: (**I**) the intensity of the emission only increases and (**II**) the intensity only decreases. In both cases, a good fit to the experimental results is obtained and the pressure dependence of some parameters is extracted, showing the direction of changes in accord with the intuitive predictions. Thus, it has been shown that (i) the ionization process of the molecule is slowed down with increasing pressure in the crystalline environment but hardly changes in the polymeric one; (ii) the efficiency of the overall hydrogen abstraction reaction of the molecules studied in the polymers decreases as pressure increases; (iii) the efficiency of the emissive photoproduct for both ketones is enhanced with increasing pressure. Finally, for DMABA we postulate the creation of two sets of conformers of the emissive photoproduct, corresponding to the change in intensity of either the light-induced phosphorescence or fluorescence.

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