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STUDY OF THE EXCITED STATES OF NAFION INCORPORATED XANTHONE AND BENZOPHENONE#

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Abstract - The photochemistry of xanthone and of benzophenone has been examined in Nafion membranes in their acid and sodium exchanged forms. Both ketones remain in their neutral form in their ground state, but in acid-Nafion they protonate upon excitation and lead to the typical fluorescence of the protonated form. Similarly, the triplet states protonate in the acid membranes. These membranes offer excellent protection from oxygen quenching.

Nafion perfluorinated membranes[1] provide a rather unique solid matrix. They consist of a carbon backbone with pendant chains terminated in sulfonate head groups which are responsible for its ion exchange and swelling properties. Nafion membranes have been compared with reverse micelles.[2] The membranes are easily swollen with polar organic solvents such as alcohols[3] and allow substrates to be incorporated into the polymer matrix. Air dried Nafion has been reported to contain 4.4% w of water,[3] which corresponds to three water molecules per $-SO_3H$ group. The membranes also provide a strongly acidic environment to the incorporated molecules.[1,4] Nafion membranes are commercially available in various forms, including transparent films, which provide a very convenient medium for solid state photochemistry. In the last few years a few photochemical systems have been examined in Nafion membranes, including $Ru(bpy)_3^{2+}$,[5-8] pyrene,[3] various organic rearrangements and isomerizations[9-13] and semiconductors.[14-15] Surprisingly, aromatic ketones, which have been studied in a wide variety of homogeneous and heterogeneous media do not appear to have been examined incorporated into Nafion; in fact, this is a particularly interesting medium, since ketone photochemistry is well known to be strongly dependent upon the acidity of the medium.[17] In particular, in the cases of xanthone and benzophenone their behaviour in acidic media have been examined in considerable detail;[17-25] these ketones serve as a rather interesting pair of probes. For example, while their molecular sizes are sufficiently similar that they can be expected to be accommodated by similar cavities, their excited states show some differences in their properties[22-24] and for example the quantum yields for fluorescence in 85% H_3PO_4 have been reported to be 0.0062 and 0.58 for benzophenone and xanthone, respectively.[17] Xanthone triplets are also well established as probes for environmental polarity.[26,28-30]

In this paper we report a study of the characteristics of xanthone and benzophenone incorporated into Nafion membranes. Aspects examined include their absorption spectra, fluorescence, phosphorescence and transient absorption. In most cases the results are compared with data obtained in H_2SO_4 solutions which serve as a control experiment.

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EXPERIMENTAL

Nafion 117 was purchased from Aldrich. The membrane was exhaustively extracted with methanol for several hours, and then dried at room temperature under vacuum. It was then allowed to equilibrate to open air. The sodium exchanged form of the Nafion membrane (Na-Nafion) was prepared by soaking the membrane in aqueous 1 M NaOH (7.5 M NaOH led to the same results) for 2 days at room temperature. It was then washed with water 3 times over a period of 24 hours, and dried in the same form as the original acid form of the film.

The membranes were swollen with 10^{-3} M solutions of the corresponding ketones for about 20 minutes and then their surface was briefly washed with methanol. The membranes were then dried and outgassed under vacuum; the samples were typically contained in 3×7 mm^2 Suprasil cells which fit into our luminescence and transient absorption equipment. Scanning electron micrographs of the films showed no sign of surface crystals on the membrane.

UV-visible spectra were recorded using an HP-8451-A diode array spectrometer. Fluorescence and phosphorescence spectra were recorded on a Perkin-Elmer LS-5 spectrofluorimeter; the same instrument was used to examine the phosphorescence lifetimes, but unfortunately the longest time that can be recorded with this instrument is limited to 10 ms. On occasion this proved too short for accurate lifetime determinations. Fluorescence lifetimes were determined using a PRA single photon counting instrument with a hydrogen filled lamp. The samples were positioned so that the plane of the film bisected the angle formed between the excitation and emission beams.

Most laser flash photolysis experiments were carried out using the pulses (308 nm, ~4 ns, ≤60 mJ/pulse) from a Lumonics TE 860-2 excimer laser filled with Xe-HCl-He mixtures; for a few experiments with xanthone the pulses (337.1 nm, ~8 ns, ≤8 mJ/pulse) from a Molectron UV-24 nitrogen laser were preferred. Further details on our laser system have been reported elsewhere.[26,31] The samples were positioned at 45° with respect to both the excitation and monitoring beams.

All H_0 acidities are based on data reported by Olah.[32]

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectra of both benzophenone and xanthone on Nafion membranes are very similar to those recorded in typical organic solvents, although on close examination minor differences are observed. For example, Figure 1 illustrates the case of xanthone, showing its spectra in methanol,

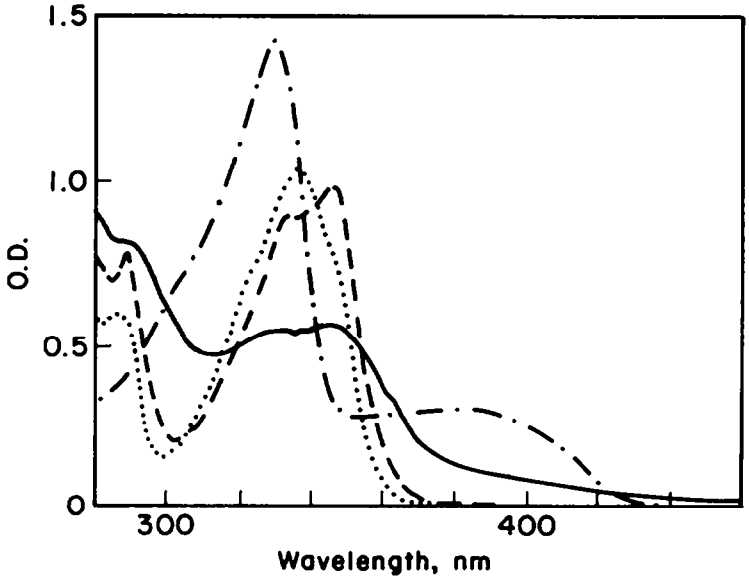

Figure 1. Ground state absorption spectra of xanthone in methanol (····), Nafion (——), Na-Nafion (----) and 50% H_2SO_4, v/v (— · — ·).

Nafion, Na-Nafion and in 50% H_2SO_4 (v/v), where the corresponding longest wavelength maxima are at 338, 346, 345, and 380 nm, respectively. Quite clearly, only in the case of H_2SO_4 solution is there a substantial shift, which should be attributed to the protonated ground state of xanthone.[24] Protonation in 50% H_2SO_4 (H_0 = -6) is not surprising, since the $pK(S_0)$ of xanthone has been

reported to be around -4.1.[24,33,34] However, absence of protonation on Nafion would indicate that the acidity experienced by the molecule is $H_0 \geq -4.1$; this appears to contrast with the estimate of $H_0 < -6.5$ made by Childs and Mika-Gibala.[18] The origin of this difference is probably in the different pretreatment of the Nafion samples, since Childs and Mika-Gibala utilized an oven and P_2O_5 dried Nafion, which the authors describe as an "anhydrous" membrane, quite different from the air-equilibrated form utilized in the preparation of our samples.

Benzophenone, with reported $pK(S_0)$ values in the -5.7 to -6.2 range[35,36] is less basic than xanthone and led to no evidence for ground state protonation under the conditions described above. We therefore conclude that both benzophenone and xanthone remain predominantly in their neutral form, in Nafion or Na-Nafion.

Fluorescence Spectroscopy and Lifetimes

Benzophenone does not fluoresce in usual organic solvents, while xanthone fluoresces weakly.[24,25] When incorporated on Nafion both ketones show fluorescence, much as they do in sulfuric acid (H_0 = -3.5). Xanthone in Nafion fluoresces with λ_{max} = 450 nm, which should be compared with solution values of 395 and 456 nm for the unprotonated and protonated forms, respectively.[24] In Na-Nafion the fluorescence from xanthone was very weak, with λ_{max} = 390 nm.

Lifetime measurements for xanthone in sulfuric acid (H_0 = -3.5) led to a single monoexponential decay with τ = 22.4 ns under nitrogen. In vacuum outgassed Nafion (20h) the decay of the fluorescence was also monoexponential with τ = 25.7 ns (Figure 2). The unprotonated form is much shorter lived, with τ ~ 3 ns.[25] When equilibrated with air only minor O_2 quenching was observed; the decay remained monoexponential with τ = 24.5 ns. The fluorescence decay of xanthone on Na-Nafion was clearly multiexponential. On a first approximation it was treated with a biexponential function (χ^2 = 4.4) and indicated that over 95% of the decay occurred with τ = 1.7 ns, with the residual 5% decaying in a more complex manner with τ ~ 8 ns. The main component is clearly comparable with that for the unprotonated form,[25] as suggested also by the fluorescence spectra.

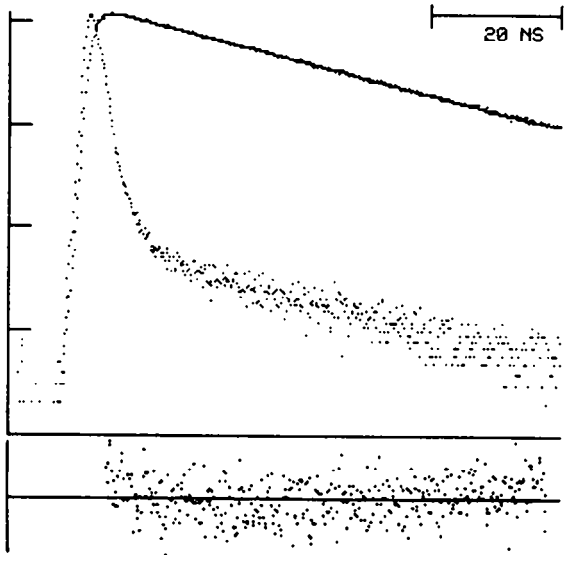

Figure 2. Single photon counting data illustrating the decay of xanthone fluorescence in Nafion, along with the corresponding excitation profile and the fit for a monoexponential decay. Bottom: Plot of weighed residuals.

Benzophenone on Nafion also shows fluorescence emission, with λ_{max} = 450 nm, and is similar, but stronger than the fluorescence in sulfuric acid (H_0 = -3.5). The reported fluorescence maximum for protonated benzophenone in various acidic media ranges from 426 nm[22] to 495 nm.[17]

The decay of the fluorescence for benzophenone on Nafion was biexponential with 3.0 ns and 9.0 ns (χ^2 = 1.2) lifetimes. The long component accounted for 40% of the decay at λ > 350 nm. Again

introduction of air into the sample did not change substantially the lifetimes (2.3 and 8.1 ns), but the long component now accounted for only 15% of the overall luminescence. The fluorescence of benzophenone in sulfuric acid was too weak to allow an accurate study of its decay kinetics.

Phosphorescence Spectra and Lifetimes

Benzophenone phosphoresces in polar organic solvents with a 0-0 band at 413 nm.[37] In acidic solutions its phosphorescence intensity is a function of acidity;[17,22] it does not show any significant phosphorescence in H_2SO_4 (H_0 = -3.5) at room temperature. By contrast, phosphorescence could be detected from both Nafion and Na-Nafion films. Figure 3 illustrates the phosphorescence spectra in these two environments and in an ethanol glass at 77 K. Quite clearly, the 0,0 bands are blue shifted in the films, their positions being 398, 399 and 414 nm for Na-Nafion, Nafion and ethanol glass, respectively. Benzophenone phosphorescence is known to undergo a blue shift in polar solvents.[37] The phosphorescence lifetime in vacuum outgassed Na-Nafion is ~26 ms, although it should be noted that this value is only based on the first 10 ms of decay (see Experimental); in any event, the value is clearly longer than the 5-6 ms lifetime reported in glassy matrices at 77 K.[37] The long lifetime in Na-Nafion membranes suggests that the probe molecules are isolated and in a rather rigid environment.

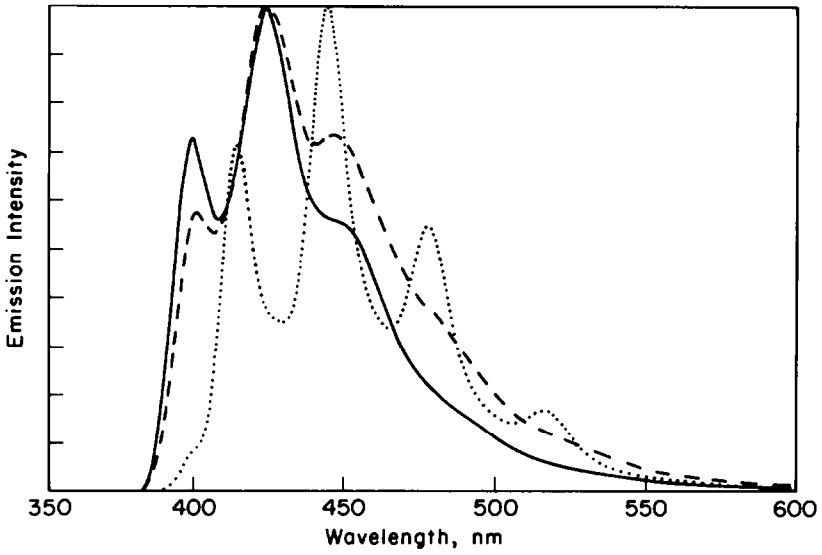

Figure 3. Phosphorescence of benzophenone at 77K in an ethanol glass (••••), Nafion (----) and Na Nafion (——). Excitation is at 330 nm.

The fact that the spectra are nearly identical in Nafion and Na-Nafion suggests that the benzophenone triplet is not protonated in Nafion at 77K. By contrast, at room temperature the Na-Nafion spectrum remains almost the same (except for a loss of resolution), while in Nafion the 399 band disappears and a new broad emission at ~470 nm is observed; this is attributed to the protonated triplet.[17] The phosphorescence of benzophenone in Nafion was much weaker than that in Na-Nafion. The weakness of the phosphorescence in Nafion is not entirely unexpected, since Ireland and Wyatt[22] have shown that in H_2SO_4 solutions the luminescence intensity drops to virtually zero for $H_0 > -5.5$; again, this sets a limit to the effective H_0 in Nafion membranes.

Xanthone showed no phosphorescence in Nafion or in H_2SO_4 (H_0 = -3.5) solution. In Na-Nafion two intense broad peaks were observed at 390 and 435 nm; both show decay lifetimes in excess of 100 ms. The excitation spectrum of both bands agrees well with the absorption spectrum of unprotonated xanthone. The 435 nm band is in the expected region for the phosphorescence of xanthone, but the presence of a 390 nm band is rather surprising. This band is likely due to delayed fluorescence.

At room temperature attenuation of the excitation beam (4 to 100%) caused no change in the relative ratio of the two peaks, suggesting that this delayed fluorescence does not arise from T-T annihilation. However, when the membrane is cooled (Figure 4) the relative intensity of the 390 nm peak decreased rapidly and at 77K this band is not present. This is consistent with delayed fluorescence by thermal population of the singlet manifold. Examination of the relative band positions and the temperature dependence of their relative intensities indicates that the S-T gap is ~4 kcal/mol, similar to the value of ~3.7 kcal/mol in solution.[37]

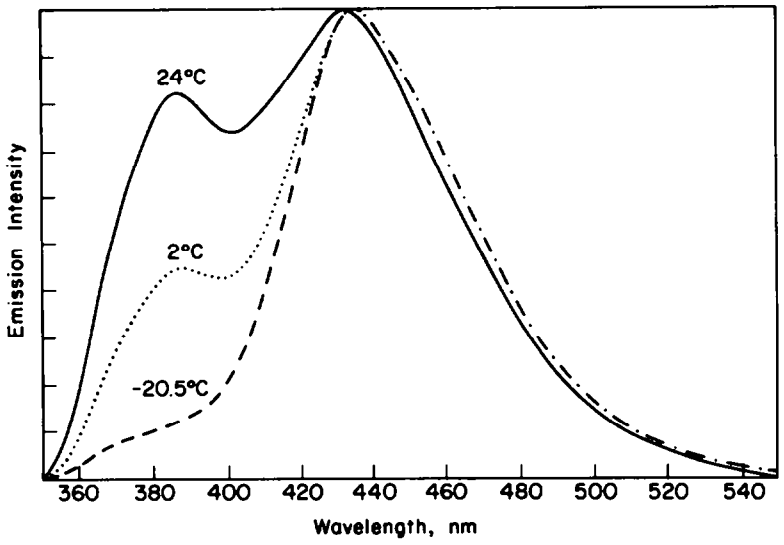

Figure 4. Effect of temperature on the luminescence of xanthone on Na-Nafion at room temperature, 2±2°C and -20.5±2°C. Excitation at 330 nm.

Laser Flash Photolysis

In organic solvent benzophenone shows triplet-triplet absorption at 525 nm (ε ~ 7640 $M^{-1}cm^{-1}$).[38] Nafion membranes are sufficiently transparent that laser photolysis experiments are straightforward. Nafion incorporated benzophenone gives a very broad T-T absorption signal (Figure 5) with maxima at 380 and 540 nm. It is likely that the 380 nm band and some underlying absorption in the 500 nm region are due to the protonated benzophenone triplet.[20] The absorption at longer wavelengths may be due to some unprotonated triplet, or more likely to ketyl radicals, presumably

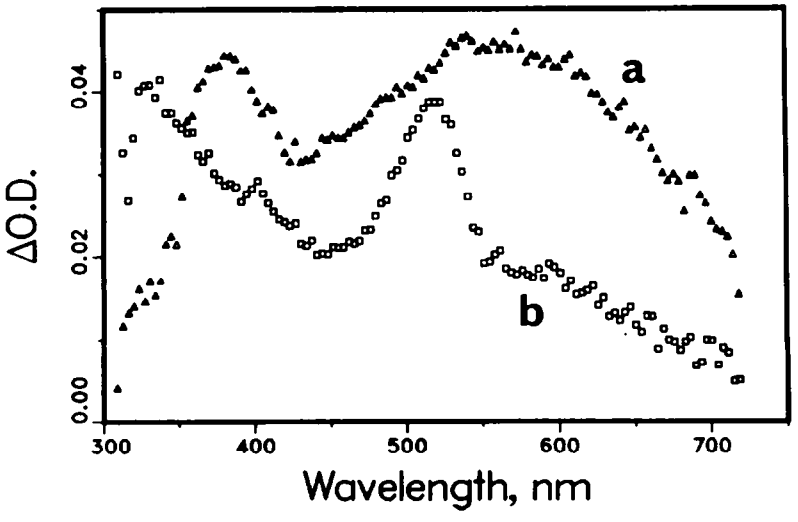

Figure 5. T-T absorption spectra for benzophenone triplet in (a) Nafion (protonated triplet) and (b) in Na-Nafion (unprotonated triplet).

generated by reaction of the triplet with residual methanol (used for the inclusion). Under oxygen-free conditions the decay lifetime (>>100 μs) is too long to be monitored in our equipment. In an air equilibrated film the lifetime is reduced to 1.1 μs and is the same at 380 and 500 nm.

In air equilibrated Na-Nafion the T-T absorption spectrum of benzophenone shows a single maximum at 520 nm (Figure 5) which agrees well with literature values of 525 nm for the unprotonated benzophenone triplet.[28] The triplet lifetime under air was (26±1 μs), while under vacuum it was ≥100 μs.

The T-T absorption of xanthone is known to be a very sensitive probe of environmental polarity;[26-30] its absorption maxima occur at 610,655,610 and 585 nm in 2-propanol, carbon tetrachloride, sodium dodecyl sulfate micelles and water, respectively.[26-30] Even in the solid state it can sense polarity differences between the hydrophobic zeolite Silicalite and silica gel, which lead to absorption maxima at 605 and 580 nm, respectively.[29] Previous studies of Nafion membranes utilized the fluorescence from pyrene as a probe for the microenvironment;[3,5] these studies suggest that the polarity experienced by the pyrene probes is intermediate between those of methanol and water for Nafion, as well as Na-Nafion.[5] In Na-Nafion the T-T absorption for xanthone occurs at 595 nm (Figure 6), indicating an environment similar to water. Nafion in its acid form leads to a new species, the protonated xanthone triplet, with λ_{max} at 530 nm (Figure 6), in good agreement with the literature value[24] in sulfuric acid solution. The intensity of the protonated absorption signal was much weaker than that in Na-Nafion. Presumably this reflects the lower quantum yield of intersystem crossing in acidic media.[17] The triplet lifetimes were too long for accurate determination in oxygen-free samples. In air equilibrated samples the triplet lifetimes were 37.5 and 9.5 μs in Na-Nafion and Nafion, respectively. Both systems were monitored at their corresponding maxima and showed simple monoexponential decay. It would appear from these lifetimes that the triplets are well protected from O_2 in many of the sites in the membrane.

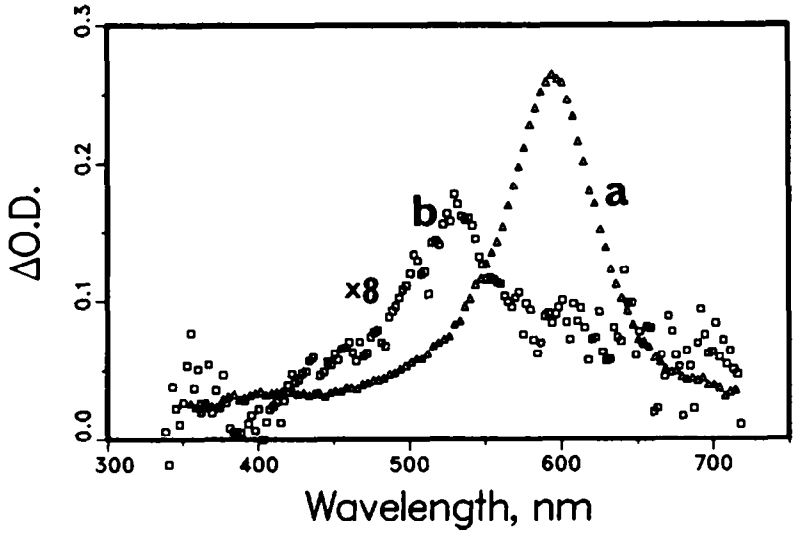

Figure 6. T-T absorption spectra for xanthone in (a) Nafion (protonated triplet) and (b) Na-Nafion (unprotonated triplet).

CONCLUSIONS

The photochemistry and photophysics of aromatic carbonyl compounds can be readily examined in Nafion membranes using a combination of luminesence and transient absorption techniques. Oxygen quenching experiments suggest the presence of well protected inclusion sites.

Overall our results suggest an acid environment with $-4 > H_o > -6$, somewhat less acidic than the value suggsted before ($H_o < -6.5$) for "anhydrous" Nafion membranes.[13]

The polarity of Na-Nafion membranes as estimated using triplet xanthone as a probe, is similar to that of water. This is actually more polar than indicated by studies using pyrene as a probe,[5]

and may be an indication that polarity is probe-dependent, which may suggest the involvement of different sites in each case.

REFERENCES

1. W. Grot, Chem. & Ind., 647 (1985).
2. R.A. Komoroski and K.A. Mauritz, J. Am. Chem. Soc., 100, 7487 (1978).
3. P.C. Lee and D. Meisel, Photochem. Photobiol., 41, 27 (1985).
4. G.A. Olah, G.K. Surya Prakash and J. Sommer, Science, 206, 13 (1979).
5. M.N. Szentirmay, N.E. Prieto and C.R. Martin, J. Phys. Chem., 89, 3017 (1985).
6. D.A. Buttry and F.C. Anson, J. Am. Chem. Soc., 104, 4824 (1982).
7. C.M. Lieber and N.S. Lewis, J. Am. Chem. Soc., 107, 7190 (1985).
8. P.C. Lee and D. Meisel, J. Am. Chem. Soc., 102, 5477 (1980).
9. G.A. Olah, M. Arvanaghi and V.V. Krishnamurthy, J. Org. Chem., 48, 3359 (1983).
10. M. Demuth, G. Mikhail and M.V. George, Helv. Chim. Acta, 64, 2759 (1981).
11. K.S. Petrakis and J. Fried, Synthesis, 891 (1983).
12. R.F. Childs, B. Duffey and A. Mika-Gibala, J. Org. Chem. 49, 4352 (1984).
13. R.F. Childs and A. Mika-Gibala, J. Org. Chem., 47, 4204 (1982).
14. A.W.-H. Mau, G.-B. Huang, N. Kakuta, A.J. Bard, A. Campion, M.A. Fox, J.M. White and S.E. Webber, J. Am. Chem. Soc., 106, 6537 (1984).
15. N. Kakuta, K.H. Park, M.F. Finlayson, A. Veno, A.J. Bard, A. Campion, M.A. Fox, S.E. Webber and J.M. White, J. Phys. Chem., 89, 732 (1985).
16. M. Krishnan, J.R. White, M.A. Fox and A.J. Bard, J. Am. Chem. Soc., 105, 7002 (1983).
17. R. Rusakowicz, G.W. Byers and P.A. Leermakers, J. Am. Chem. Soc., 93, 3263 (1971).
18. G. Favaro, J. Photochem., 15, 89 (1981).
19. G. Favaro, Chem. Phys. Lett., 31, 87 (1975).
20. H. Shizuka and E. Kimura, Can. J. Chem., 62, 2041 (1984).
21. G. Favaro and G. Bufalini, J. Phys. Chem., 80, 800 (1976).
22. J.F. Ireland and P.A.H. Wyatt, J. Chem. Soc., Faraday Trans. I, 69, 161 (1973).
23. D.M. Rayner and P.A.H. Wyatt, J. Chem. Soc., Faraday Trans. II, 70, 945 (1974).
24. J.F. Ireland and P.A.H. Wyatt, J. Chem. Soc., Faraday Trans. I, 68, 1053 (1972).
25. B.S. Vogt and S.G. Schulman, Chem. Phys. Lett., 97, 450 (1983).
26. J.C. Scaiano, J. Am. Chem. Soc., 102, 7747 (1980).
27. A. Garner and F. Wilkinson, J. Chem. Soc., Faraday Trans. II, 72, 1010 (1976).
28. F. Wilkinson and A. Garner, Photochem. Photobiol., 27, 659 (1978).
29. F. Wilkinson, C.J. Willsher, H.L. Casal, L.J. Johnston and J.C. Scaiano, Can. J. Chem., 64, 539 (1986).
30. J.C. Scaiano and J.S. Selwyn, Can. J. Chem., 59, 2368 (1981).
31. J.C. Scaiano, M. Tanner and D. Weir, J. Am. Chem. Soc., 107, 4396 (1985).
32. G.A. Olah, "Friedel-Crafts Chemistry", Wiley, New York (1973), p. 368.
33. A.I. Tomachev, L.N. Shulezhko and A.A. Kisilenko, Z. Obsch. Khim., 35, 1708 (1965).
34. I. Degani, R. Fochi and G. Spunta, Boll. Sci. Fac. Chim. Ind. Bologna, 26, 3 (1968).
35. A. Fischer, B.A. Grigor, J. Packer and J. Vaughan, J. Am. Chem. Soc., 83, 4208 (1961).
36. T.G. Bonner and J. Phillips, J. Chem. Soc. B, 650 (1966).
37. S.L. Murov, "Handbook of Photochemistry", Dekker, New York (1973), p. 41.
38. I. Carmichael and G.L. Hug, J. Phys. Chem. Ref. Data, 15, 1 (1986).