Violet Sensitive Acid Generator and Its Photoacid Generation Efficiency [a]

ZHANG Wei-Min, WANG Jian, WANG Wen-Guang and PU Jia-Ling [b]; Lab. of Printing & Packaging Material and Technology, Beijing Institute of Graphic Communication, No.25, Xinghua Beilu, Huangcun, Daxing; Beijing 102600, P. R. CHINA

Abstract

In this paper, a series of violet sensitive photoacid generators (PAG) were prepared and their photoacid generating behaviors were investigated spectrophotometrically. Rhodamine B, an acid sensitive dye, was used to trace quantitatively the acid produced upon irradiation. Experiment results showed photodecomposition of PAG and the consequent acid forming process were mainly determined by PAG's chemical structure and types of solvent used, irrespective of the concentration of PAG. Almost all the PAGs investigated became photo-inert and did not decompose when THF was used as the solvent. Quantum yield of photodecomposition was found nearly equal to that of acid formation, indicating that active species produced by the PAG upon irradiation were almost 100% converted to acids.

1. Introduction

Photoacid generators, as a key element, are widely used in imaging systems based on acid sensitive materials. In most cases, the system consists of a photoacid generator and a acid sensitive polymer. In the imaging process, photoacid generator produces acid upon irradiation, which in turn induces or catalyzes the polymer to decompose, and as a result, deliquescent differences are created between the exposed area and unexposed areas. The differences are developed into images by post washing treatment with suitable solution. Imaging seed is heavily dependent on the quantum yield of photoacid generation. If an acid proliferation generator is further added in this system, larger acid quantum yield and consequently higher sensitivity and imaging speed are expected. Photoacid based imaging system is, therefore,an imaging system which may amplify the effect of exposure offering high sensitivity and is finding wide applications in micro-electronics, large-scale molectron [1-4].

Quantitative evaluation of quantum yield of photoacid generation is of key importance and provides decisive information to the design of photoacid generator and the related material system [7-8]. A spectrophotometry which uses Rhodamine B as an acid sensitive indicator to trace quantitatively the acid produced upon irradiation have found wide applications and proved to be a valid method in quantitative assessment of photoacid generation for a great number of PAGs [5-6]. This method was also employed in this work to quantitatively investigate the new PAGs which were synthesized in our lab and to check their effectiveness as PAGs for laser imaging at 405 nm.

2. Evaluation of Photodecomposition and Photoacid Generation Efficiencies

(1)Standard Working Curve

Rhodamine B, an acid sensitive dye, was weighed and dissolved in certain volume of solvent (e.g., Acetonitrile, THF, $CHCl_3$) and then, an acid (e.g, TFSA, HCl or other types of acids) was added at different concentrations. A series of Standard Working Solutions of acid were thus obtained and their electronic absorption spectra were recorded by using a commercial UV-vis spectrophotometer. A new absorption peak was produced by acid and its ABS at 555 nm was taken and plotted against the acid concentration to give the Standard Working Curve. Fig1 shows that the absorption peak of Rhodamine B at 555nm increased with increasing acid concentrations.

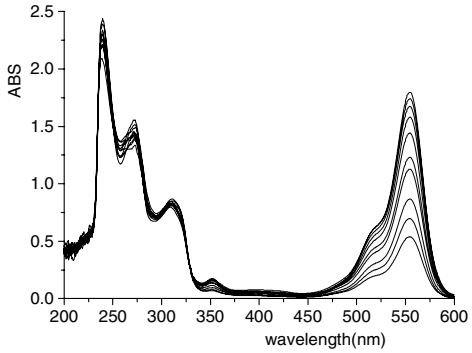

Fig1. Electronic absorption spectra of Rzhodamine B at different acid concentrations

(2) Determination of Photodecomposition Efficiency

A weighed PAG was completely dissolved in Acetonitrile or THF and then the solution was exposed to 405nm monochromatic radiation for a certain period of time. The light intensity was fixed at 0.4mW/cm^2. Electronic absorption spectra of the exposed solution were recorded by a commercial UV-vis spectrophotometer. ABS and its difference ΔABS with exposed time at the wavelength corresponding to the actinic absorption peak of PAG were taken and fed into Equation 1 to calculate photodecomposition efficiency or quantum yield of photodecomposition of PAG.

$$\Phi_{PD}= \frac{(\Delta ABS/\varepsilon \times L) \times V \times N_A}{I \times (1-e^{-ABS}) \times S \times t/h\nu} \qquad (1)$$

Where ΔABS is absorbency difference, ε is molar extinction coefficient, L is the effective sample length, V is the effective sample volume, S is the exposed effective sample area, N_A is molar constant, I is light intensity, t is exposure time and hν is photon energy.

(3) Determination of Photoacid Generation Efficiency

Solution similar to the Standard Working Solution but with the acid replaced by a PAG was prepared and exposed to 405nm monochromatic radiation in the same way as described above. Absorbance difference at 555 nm was taken and then fitted in the Standard Working Curve to find the corresponding acid concentration. Quantum yield of photoacid generation could be calculated using following equation:

$$\Phi_{PAG} = \frac{C \times V}{N_P} \qquad (2)$$

Where C is acid concentration determined as above, V is effective sample volume and N_P is the number of photon absorbed.

3. Experimental

(1) Reagents and Instrumentals

Trifluoromethyl sulfonic acid (TFSA), HCl, Rhodamine B and solvents were commercially obtained and purified and dehydrated before use. The PAG used in this paper, i.e. PAG1, was synthesized in our lab, the structure of which was shown in Fig. 2. Electronic absorption spectra were measured with SHIMADZU UV-2501PC spectrophotometer and fluorescence spectra were was measured with SHIMADZU RF-5301PC spectrofluorophotometer. Light intensity was measured by using Gamma Scientific's Digital Radio/Photometer DR-1600. Exposure device was home made. 365nm and 405nm monochromatic radiations were obtained by inserting a suitable interference filter between the sample and a 400 W high pressure mercury lamp.

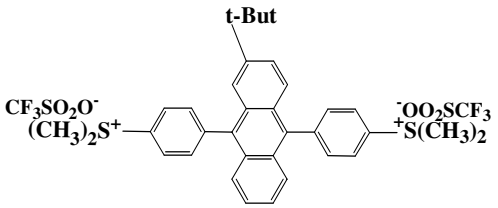

Fig.2 The structure of PAG1

(2)Determination of Acid Concentration of Standard Working Solution

Considering that the PGAs in this study might generat either TFSA or HCl when being exposed to UV-visable irradiation, so TFSA and HCl solutions with different concentrations were prepared and used for comparison to determine whether the PAG release acid and how much acid be produced. The acid concentrations of TFSA and HCl solutions were determined with non-aqueous titration method in which a combination of diphenyl-guanidine solution of known concentration and dimethyl yellow (the indicator) was used.

4. Results and Discussion

(1)Standard Working Curve

Fig. 3 shows the Standard Working Curve for TFSA and HCl in acetonitrile and a very good linear relationship between the absorbence difference and acid's concentration was found.

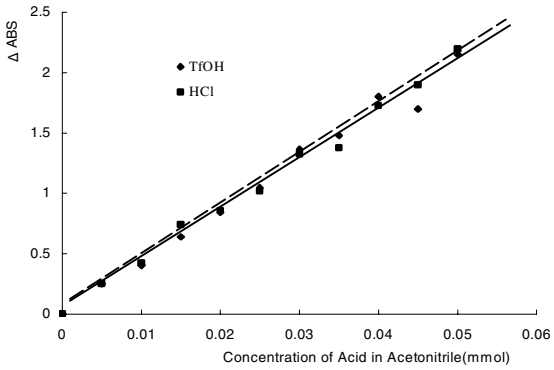

Fig. 3 Standard working curve

(2) Photodecomposition of PAG and Its Solvent Dependence

Photodecomposition of PAGs were found strongly dependent on solvent. Photodecomposition occurred effectively in acetonitrile, but quenched completely when acetonitrile was replaced by dimethylsulfoxide, THF and even the mixture of acetonitrile and THF. Strong emission of fluorescence by PGAs were observed in dimethylsulfoxide, THF and the mixure of acetonitrile and THF, but disappeared when the solvent was replaced by acetonitrile. This result indicated that fluorescence emission was the overwhelming channel through which the electronically excited PAGs gave up their extra electronic energies in solvent like dimethylsulfoxide, THF and the mixure of acetonitrile and THF, but chenmical decomposition dominated the physical process of fluorescence emission in solvent like acetonitrile. Acetonitrile apparently participated in some way in and greatly facilitated the chemical decomposition of the excited PAGs.

(3) Influence of PAG's Concentration on Photodecomposition Efficiency

Data of photodecomposition efficiency of PAG at different concentrations were listed in Table 1. The data fluctuated around an average value of 0.201 within a narrow range of + 0.008 and – 0.006, indicating that photodecomposition remained virtually constant regardless of PAG's concentration.

Table1. Dependence of Photodecomposition Efficiency on PGS Concentration

Concentration (mmol/l)	0.175	0.144	0.100	0.058	0.020
Φ_{PD}	0.210	0.190	0.206	0.210	0.195

Note: Data for PAG in acetonitrile; irradiation was at 405 nm

Photodecomposition efficiency of PAG1 at different wavelength was given in Table 2. PAG1 had three absorption peaks at 357 nm, 372 nm and 392 nm, respectively. As revealed by Table 2, photodecomposition efficiency at 405 nm was nearly ten times larger than at 365nm, indicating that the longer wavelength peak of PAG1 was its most actinic absorption peak.

Table 2 Photodecomposition Efficiency of PAG at Different Wavelenth

λ(nm)	I(W/cm^2)	Φ_{PD}
405	0.53×10^{-4}	**0.19**
365	7.54×10^{-4}	**0.017**

Note: Data for PAG in acetonitrile; irradiation was at 405 nm

(4) Photoacid Generation Efficiency and Its Dependence on Concentration

Table3. Φ_{PAG} and Its Dependence on PAG's concentration

Concentration(mmol/l)	0.087	0.058	0.024	0.02
Generating Efficiency	0.195	0.190	0.200	0.195

Photoacid generation efficiency of PAG1 in acetonitrile was provided in Table 3 as a function of its concentration. It was obviously that photoacid generation efficiency fluctuated around an average value of 0195 and was virtually independent of PGA's concentration. The averaged ratio of Φ_{PAG} and Φ_{PD} was equal to 0.97, indicating that over 97% of photodecomposed PAG was converted to acid. This result held true to other ten types of PAGs that were prepared in our lab, though they had difference chemical structure and absorption characteristics.

5. Conclusion

From the results of this study, it was concluded that the spectrophotometrical method based on the use of Rhodamine B was a reliable one in the current study and photodecomposition of PAG and the consequent acid forming process were mainly determined by PAG's chemical structure and types of solvent used, irrespective of the concentration of PAG. Almost all the PAGs investigated became photochemically inert and did not decompose when THF or dimethylsulfoxide was used as or included in the solvent. Quantum yield of photodecomposition was found nearly equal to that of acid formation, indicating that active species produced by the PAG upon irradiation were almost 100% converted to acids.

References

[1] John L.Dektar and Nigel P.Hacker Photochemistry of Triarylsulfonium Salts.J Am.Chem.Soc.1990,112,6004-6015

[2] Wenhui Zhou,Stephen M.Kuebler,Dave Carrig,Joseph W.Perry,and Seth R.Marder.Efficient Photoacids Based upon Triarylamine Dialkylsulfonium Salts.J.AM.CHEM.SOC.2002,124(9),1897-1901

[3] F.D.Saeva,D.T.Breslin,and H.R.Luss.Intramolecular Photoinduced Rearrangements via Electron-Transfer-induced,Concerted Bond Cleavage and Cation Radical/Radical Coupling.J.AM.Chem.Soc.1991,113,5333-5337

[4] F.D.Saeva,Edwin Garcia,P.A.Martic.Comparative photochemical behavior of some anthracenyl and naphthacenyl sulfonium salt derivatives.Journal of Photochemistry and Photobiology A:Chemistry 1995,86,149-154

[5] James F.Cameron,Nicholas Chan,Kathryn Moore and Gerd Pohlers.Comparison of Acid Generating Efficiencies in 248 and 193nm Photoresists.Comparison of Prc.SPIE.2001,4345,106-117

[6] Haruyuki OKAMURA,Koichi Sakai,Masohiro Tsunooka,and Masamitsu Shirai.Journal of Photopolymer Science and Technology.2003,16(5),701-706

[7] Mitsuhiro Yanagita,Izuo Aoki,and Sumio Tokita.13C NMR and Electronic Absorption Spectroscopic Studies on the Equilibrium between the Colorless Lactone and the Colored Zwitterion Forms of a Fluoran-Based Black Color Former.Bull.Chem.Soc.Jpn.,1997,70,2757-2763

[8] Sumio Tokita,Kenji Nagahama and Fumihiro Watanable.Molecular Design for Low Radiation Dose Detection with Functional Dyes.Journal of Photopolymer Science and Technology.2000,13(2),187-190

[a] *The work was supported by Beijing Municipal Education Commission (NO. KM200610015004);*

[b] *To whom correspondence should be addressed.*

Author Biography

Zhang Wei-min, male, associate professor, graduated in East China University of Science & Technology in 1986. He is working in Lab. Printing & Packaging Material and Technology(Beijing area major laboratory), in Beijing Institute of Graphic Communication. His work is focused on organic information recording materials, especially organic photoreceptor, functional materials.