Thermochimica Acta
Elsevier Publishing Company, Amsterdam
Printed in Belgium

THERMAL ANALYSIS OF THE PHOTOSENSITIZER 2,6-BIS(*p*-AZIDOBENZYLIDENE)-4-METHYLCYCLOHEXANONE

KIM RITCHIE AND CECILE MALKIEWICZ
Motorola Inc., Semiconductor Products Division, Phoenix, Arizona (U.S.A.)

(Received October 16th, 1969)

ABSTRACT

Azides are often used as sensitizers in photographic processes. One frequently used azide sensitizer which has not been studied extensively is 2,6-bis(*p*-azidobenzylidene)-4-methylcyclohexanone (ABC). This study was undertaken to determine the effects of u.v. irradiation and solvent on the thermal behaviour of ABC. The results demonstrate the value of thermal analysis in detecting structural changes caused by solvents and chromophoric changes caused by u.v. irradiation of the azide.

INTRODUCTION

Dynamic thermal methods of analysis are becoming increasingly important techniques for the study of materials. In recent years, emphasis has been placed on employing instrumentation to develop unique methods of investigation, such as infrared spectroscopy (i.r.), electron paramagnetic resonance (e.p.r.), mass spectrometry, X-ray techniques, *etc.*

Although azides are often used as sensitizers in photographic processes, the thermal behavior of 2,6-bis(*p*-azidobenzylidene)-4-methylcyclohexanone, hereafter known as ABC, has not been reported. It is the intent of this report to discuss a study undertaken to determine the properties of the solid state of ABC. The solution chemistry of ABC and its stereochemistry will not be covered in this report.

Our study of ABC may be divided into three separate phases as follows: (*1*) thermal stability, ABC is very sensitive to temperatures greater than 30°; (*2*) Structural change, ABC can undergo polymorphic modification by the treatment of organic solvents; (*3*) Electronic effects, ABC can also undergo electron delocalization by u.v. irradiation without a change in its molecular structure. The u.v. irradiated ABC shows a thermal spectrum different from that of non-irradiated ABC. These changes can also be detected by e.p.r. but not by i.r. spectroscopy or X-ray diffraction. This study not only determines the thermal behavior of ABC but also demonstrates the capability of thermal analysis for detecting an effect due to electron shift in a molecule (free radical).

EXPERIMENTAL

ABC is prepared by precipitating the reaction product from a mixture of 16.1 g

(0.1 mole) of 4-azidobenzaldehyde and 5.5 ml (0.05 mole) of cyclohexanone in 100 ml of methanol and 5 ml of 25% KOH[1]. The precipitate was washed with methanol and water, then dried under nitrogen. This final product of yellow crystals was designated ABC_M. When ABC_M was dissolved in an organic solvent and dried under nitrogen it yielded reddish-brown crystals which were designated ABC_S. When ABC_M or ABC_S was irradiated under a 200-watt PEK Hg lamp with an intensity of 980 lumen/cm^2, it yielded dark reddish-brown crystals designated as ABC_{MUV} and ABC_{SUV} respectively.

The primary instruments used were the DuPont Differential Thermal Analyzer (900) with the Differential Scanning Calorimeter cell (DSC) and the Thermogravimetric (950) Analyzer (TGA). To support the results of these instruments i.r. and u.v. spectra were obtained from the Beckman IR-4 and DB-G, respectively. X-ray diffraction patterns were run on a Norelco diffractometer. E.p.r. and wide-line n.m.r. were obtained from Varian Associates.

The DSC and TGA runs were made in dry air atmosphere with sample size and heating rates indicated in each figure. On the DSC, samples of varying weights were run with no apparent difference in the thermal spectra. Samples were run with a hermetic and non-hermetic seal of the aluminum pans, again with no apparent difference. The aluminum sample pan was compared with the pyrex sample tube in DTA, with no apparent difference.

For thermal stability studies the DSC cell was used. The samples were first kept in an isothermal mode at 120°C for one hour, allowed to cool naturally to room temperature, then run under standard DSC conditions indicated in each figure. The samples were also run at a very slow heating rate of 5°/min as opposed to the standard heating rate of 20°/min.

DISCUSSION AND RESULTS

The photoresist sensitizer, ABC, displays two crystalline forms: red prisms and yellow needles. Both forms melt at 131–132°C when the crystals are heated rapidly.

It has been shown that many light sensitive solid phase reaction mechanisms relate to the crystalline structure of the reactants. For instance, Cohen and Schmidt investigated the photochemical behavior of cinnamic acid[2]. The different precipitation procedures yield two different crystalline forms, α and β (β form is metastable). By X-ray diffraction method, Schmidt showed that the photo-active structure of cinnamic acid can be correlated to the packing arrangements of nearest-neighbor in the monomer lattice. Our study was carried out first to obtain the thermal stability of two ABC crystalline forms and secondly to determine the ability of the thermal analyzer to distinguish the lattice structure of ABC crystalline forms. The following discussion will be divided into three separate parts, structural change, thermal stability, and electronic effect.

Structural change

Fig. 1 shows DSC curves for ABC_M and ABC_S. The endothermic peak tempera-

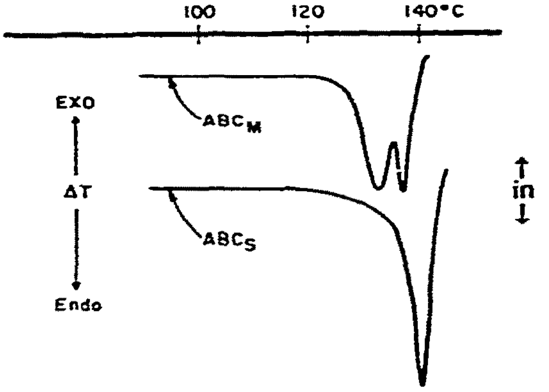


Fig. 1. DSC of ABC; rate, 20°/min; sample size, 2.0 mg; atmosphere, air; ΔT, 0.5°/in.

ture of ABC$_S$ is slightly higher and has only one peak while ABC$_M$ has two peaks. Many solvents were used to convert ABC$_M$ to ABC$_S$, among these were xylene, acetone, methanol, $CHCl_3$, CCl_4 and trichloroethylene. Attempts to convert ABC$_S$ to ABC$_M$ with solvent treatments were unsuccessful. ABC also exhibits a large exothermic peak which is shown in Fig. 2. The exothermic curve shows a shoulder that suggests two possible exothermic peaks. The TGA curve (Fig. 2) also shows two slopes of the weight loss. The weight loss may be due to the thermal elimination of nitrogen. At present the gas effluent has not been directly identified as nitrogen, but it indirectly was confirmed by the disappeareance of the 2140 cm^{-1} (4.73 μ) azide peak

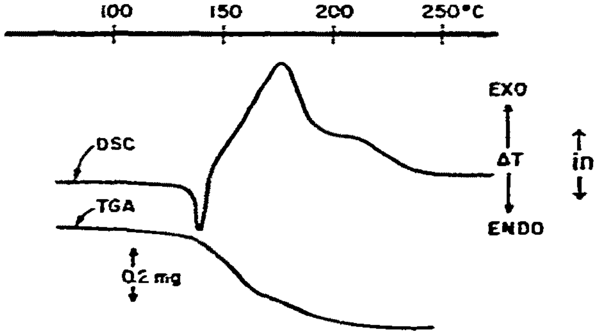


Fig. 2. Thermal decomposition of ABC$_S$; TGA—rate, 20°/min, sample size, 2.58 mg; DSC—rate, 20°/min, sample size, 1.0 mg; ΔT, 1.0°/in.

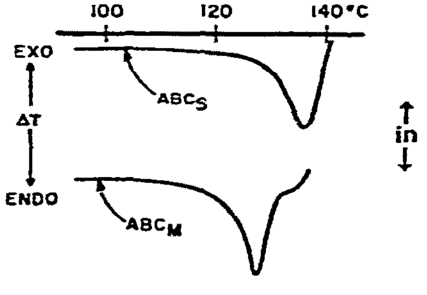


Fig. 3. U.V. irradiated ABC; DSC—rate, 20°/min; sample size, 2.0 mg; ΔT, 0.5°/in.

from the i.r. spectrum. The TGA results (Table I) are also in good agreement with the theoretical values: two moles of nitrogen per mole of ABC.

TABLE I

THERMAL DATA OF ABC

Thermal mode	*ABC type*	*ΔH endo (kcal/mole)*	*ΔH exo (kcal/mole)*
DSC	ABC$_M$	6.8	100.0
DSC	ABC$_S$	6.5	112.1
DSC	ABC$_{MUV}$	4.8	107.1
DSC	ABC$_{SUV}$	4.3	—
DSC[a]	ABC$_M$	—	80.8
DSC[a]	ABC$_S$	—	56.5
DSC[a]	ABC$_{MUV}$	—	48.8

Thermal mode	*ABC type*	*% Theoretical wt. loss*	*% Experimental wt. loss*
TGA	ABC$_M$	16.1	16.2
TGA	ABC$_S$	16.1	15.5
TGA	ABC$_{MUV}$	16.1[b]	16.1

[a] Samples were kept at 120°C for one hour before the normal procedure. [b] This value was calculated with assumption that there was no molecular-weight change by u.v. irradiation.

Also, both the X-ray diffraction spectra, Fig. 4, and the i.r. spectra, Fig. 5, show a definite structural difference between ABC$_M$ and ABC$_S$. ABC$_M$ and ABC$_S$ were also exposed to the wide-line n.m.r. spectrophotometer. The compounds have quite similar spectra, *i.e.*, the peak-to-peak distance is about 12 gauss at 70°C for both samples. However, at 100°C the signals have indicated some narrowing down to approximately 9 gauss for ABC$_M$ and 5 gauss for ABC$_S$. These effects may be due to the molecular movement[3].

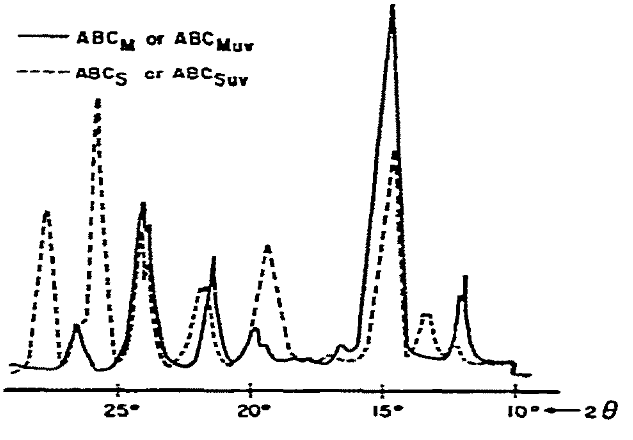


Fig. 4. Powder X-ray diffraction of ABC.

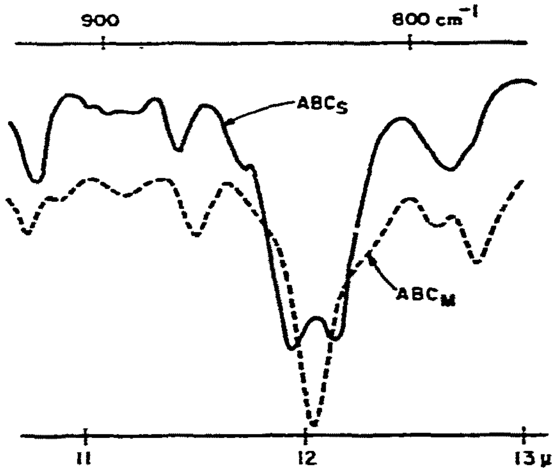


Fig. 5. I.r. spectra of ABC (KBr).

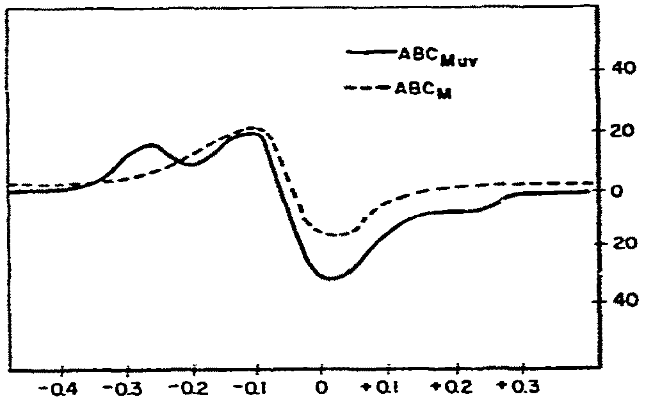


Fig. 6. E.p.r. spectra of ABC; scan range, X100G; time constant, 1 sec; microwave power, 10 mW; field set, 3398G, scan time, 2 min.

Thermal stability

The thermal stability of ABC was studied using the procedures given in the experimental section. First the isothermal mode and then a very slow heating rate mode were employed. The DSC curves of ABC_M and ABC_S, Fig. 7, are the first

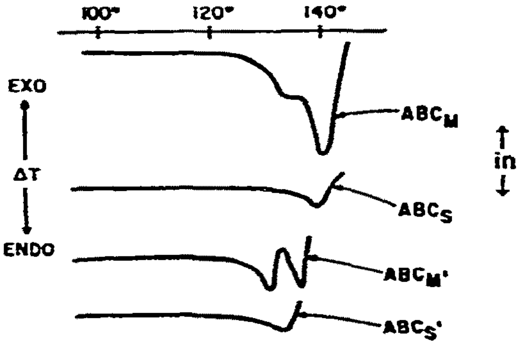


Fig. 7. Thermal stability studies of ABC on DSC. ABC_M, ABC_S — rate, 20°/min, sample size, 2.0 mg, ΔT, 0.5°/in (preheated at 120°C for 1 h); $ABC_{M'}$, $ABC_{S'}$ — rate, 5°/min, sample size, 2.0 mg, ΔT, 0.5°/in.

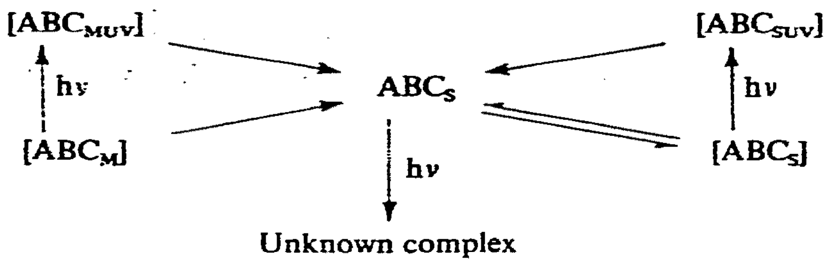
condition. The results indicate thermal instability of ABC, especially ABC_S. The results of the second condition, Fig. 7, $ABC_{M'}$ and $ABC_{S'}$ also indicate thermal instability. All the conditions on DSC programing being equal, if the heating rate is decreased then ΔH should be increased provided there were no thermal changes on the compound. According to Fig. 7, the slower heating rate (5°/min) shows a smaller ΔH of ABC fusion endotherm than the faster heating rate (20°/min) shown in Fig. 1. ABC is very sensitive to heat, and a possible oxygen adduct was also noted by TGA as low as 30°C. This phenomenon appears to be a surface reaction of crystalline ABC.

Electronic effect

Table I shows the ΔH values of ABC endotherms and exotherms. The heat of fusion endotherm of u.v. irradiated ABC is less than the non-irradiated. The DSC of u.v. irradiated ABC, Fig. 3, shows a marked difference from the endothermic peak of non-irradiated ABC (Fig. 1) as a shift into lower temperature. These changes are apparently not due to a structural change but due to an electronic change resulting from u.v. irradiation. The X-ray diffraction spectra, Fig. 4, showed a definite structural difference between ABC_M and ABC_S, but showed no difference between ABC_M and ABC_{MUV} or ABC_S and ABC_{SUV}. The electronic changes caused by u.v. irradiation on ABC_M are not only demonstrated by DSC but also by e.p.r. E.p.r. spectra, Fig. 6, show the electron delocalization of the nitrogen atom. The concentration of radicals is approximately 10^{16} spins more for ABC_{MUV} than for the non-irradiated ABC_M[3].

The u.v. irradiation of ABC appears to have no effect on the molecular structure which was shown above in Fig. 4. This was also demonstrated by u.v. spectrophotometric analysis of solutions prepared by dissolving exact amounts of ABC_{MUV} and ABC_{SUV}. The wave maximum and extinction coefficient of ABC_{MUV} or ABC_{SUV} is identical to the values of ABC_S.

The following scheme may be summarized as the polymorphic modifications of ABC. The solid state is indicated by [ ].



The elemental analysis of ABC_M, ABC_S, ABC_{MUV}, and ABC_{SUV} are shown below. This is also a good indication that these polymorphic modifications have identical molecular weights ($C = 68.53 \pm 0.20$, $H = 4.86 \pm 0.15$, $N = 22.00 \pm 0.25$).

CONCLUSION

ABC_M can undergo a topochemical change to ABC_S by treatment with organic solvents. Electron delocalization of ABC by u.v. irradiation occurs without a change in molecular structure. The electron delocalized ABC is stable until dissolved in solvent. ABC is very sensitive to temperatures greater than 30 °C. The thermal analyzer can be a useful instrument to demonstrate molecular structural changes and electron delocalization.

ACKNOWLEDGMENTS

ABC was supplied by the photoresist laboratory section of Motorola Central Research Laboratories. E.p.r. and wide-line n.m.r. spectroscopic work were done by Drs. W. C. Landgraf and L. O. Andersson of Varian Associates and their stimulating discussions are appreciated. We also appreciate discussions and encouragements of Dr. W. L. Hunter.

REFERENCES

1 I. J. SAGUNA AND J. A. VAN ALLEN, *Azide sensitized resin photographic resist*, U. S. Patent 2,940,853 (1960).
2 M. D. COHEN AND G. M. J. SCHMIDT, *J. Chem. Soc.*, 1966 (1964).
3 Private communications with Drs. W. C. LANDGRAF AND L. O. ANDERSSON of Varian Associates, Palo Alto, California, U.S.A.