

Rotational Photoisomerization of a Thioamide, N-5-Trifluoromethyl-6-methoxy-1-thionaphthoyl-N-methylglycine

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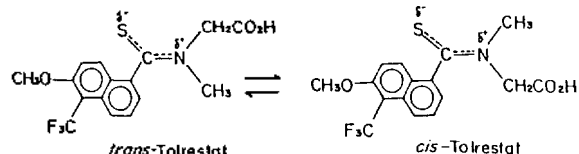
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A thioamide, N-5-trifluoromethyl-6-methoxy-1-thionaphthoyl-N-methylglycine, undergoes *trans*→*cis* photoisomerization around C-N bond in solution. Azulene quenching studies showed the photoisomerization to proceed *via* both singlet and triplet excited states. The total quantum yield of the *trans*→*cis* photoisomerization is about 0.26, 0.14 from the singlet excited state and 0.12 from the triplet excited state. Intersystem crossing and internal conversion quantum yields were calculated from sensitized photostationary state and a plausible mechanism is proposed.

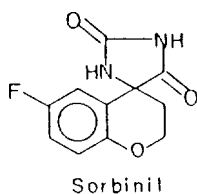
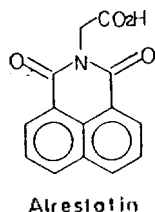
Introduction

A thioamide, N-5-trifluoromethyl-6-methoxy-1-thionaphthoyl-N-methylglycine (tolrestat, compound I), was shown to exert aldose reductase (AR; the key enzyme involved in the conversion of hexose to polyols) inhibitory activity, and it is useful for the treatment of diabetic complications.¹⁻⁷

Thioamides are stable in the solid state, but they exist as conformational equilibrium mixtures in solution.⁸ Conformational isomerism of thioamides as a result of hindered rotation about the C-N bond is well-known phenomenon.⁹⁻¹⁴ The title compound undergoes thermal isomerization around C-N bond ($E_a = 25-26$ kcal/mol) and exists as the equilibrium mixture of rotational isomers.¹⁵



Alrestatin¹⁶⁻¹⁷ and sorbinil^{2, 18-20} as well as tolrestat are reported as the inhibitors of aldose reductase. In vitro, using aldose reductase from bovine lenses, tolrestat exhibited more potent activity than alrestatin and sorbinil.²⁰ Assuming that these compounds inhibit aldose reductase by interacting with the same site on the enzyme,²¹ the difference in intrinsic activity suggests that the conformationally more flexible tolrestat adapts to the steric requirements for aldose reductase inhibition more readily than do the structurally rigid alrestatin and sorbinil.²⁰



Compound I undergoes conformational photoisomerization in the presence of day light. In this investigation, the mechanism of conformational photoisomerization and photo-physical properties of Compound I are studied since the results of conformational photoisomerization can serve as a basis for optimal design of appropriate dosage forms and as a

Table 1. The effect of Azulene on the *trans*→*cis* Photoisomerization of Compound I at 366 nm in Ethanol Solution^a

[Az] × 1000	Φ_{fc}	Φ^0/Φ	Φ^1	Φ^1/Φ_3
0.00	0.26	1.00	0.12	1.00
0.40	0.24	1.08	0.10	1.20
0.80	0.23	1.13	0.09	1.33
2.00	0.21	1.24	0.07	1.71
4.00	0.19	1.37	0.05	2.40
6.00	0.18	1.44	0.04	3.00
8.00	0.17	1.53	0.03	4.00

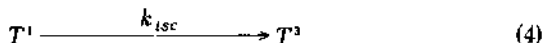
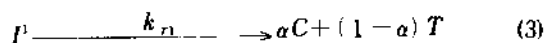
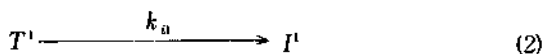
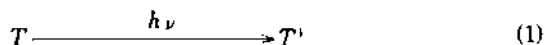
^aConcentration of I is 7.4×10^{-3} M; All photoreactions are carried out at room temperature and all data are corrected for thermal isomerization reactions (about 1-2 %). ^bCalculated with $\Phi^0 = 0.14$.

background for biopharmaceutical studies of tolrestat.

Results and Discussion

The compound I in ethanol solution showed no detectable emission (fluorescence or phosphorescence) at room temperature, while strong phosphorescence ($\lambda_{max} = 513$ nm) was observed with quantum yield of 0.48 ± 0.02 at 77 K. No fluorescence was detected even at this temperature. From the 0-0 band of phosphorescence spectrum, triplet energy is determined to be 56 kcal/mol.

The *trans*→*cis* photoisomerization reaction was carried out in ethanol solution to low conversion (lower than 10 %) and the photoisomerization is quenched by azulene as summarized in Table 1. The Stern-Volmer plot (Figure 1) is curved suggesting that the photoisomerization proceeds *via* both excited singlet and triplet states.²³ The following photoisomerization mechanism involving both singlet and triplet excited states is proposed (eq's 1-6).



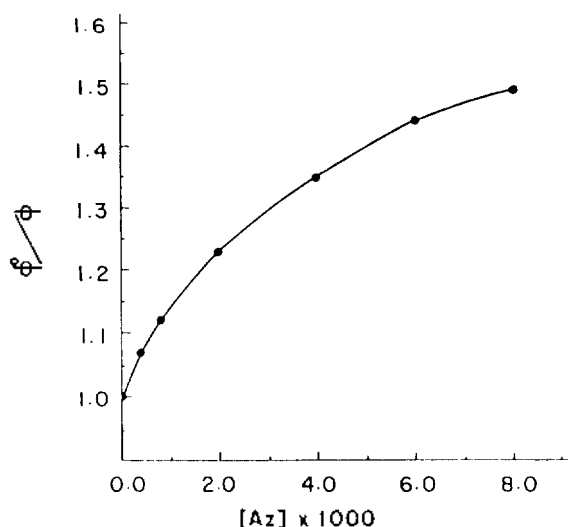


Figure 1. Azulene quenching of the photoisomerization of compound I at 366 nm in ethanol.

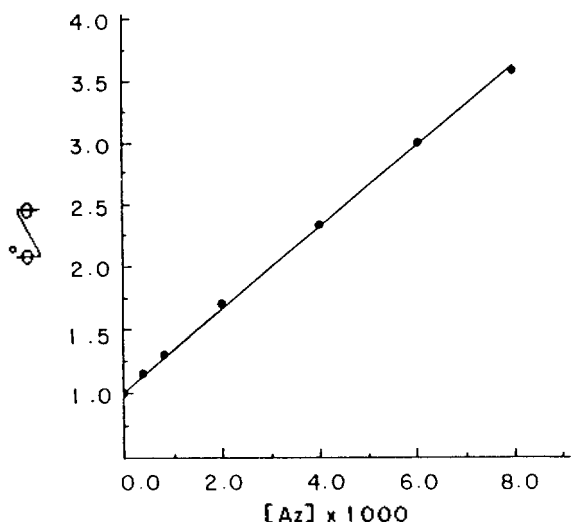
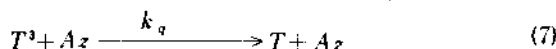
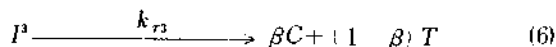
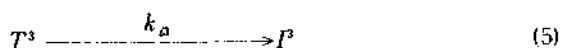


Figure 2. Azulene quenching of the photoisomerization of compound II (Tolrestat) via triplet excited state at 366 nm in ethanol.



where T; *trans*-tolrestat, C; *cis*-tolrestat, I^3 ; triplet intermediate, I^1 ; singlet intermediate, α ; the portion of isomerization from I^1 , β ; the portion of isomerization from I^3 . In this mechanism, only one excited state, the triplet excited state, is quenched by azulene.

$$\Phi_1^0 = \frac{\alpha k_a}{k_d + k_{isc}} = \tau_1 \alpha k_a \quad (8)$$

$$\Phi_3^0 = \frac{\beta k_{isc}}{k_d + k_{isc}} = \beta \Phi_{isc} \quad (9)$$

$$\Phi^0 = \Phi_1^0 + \Phi_3^0 = \alpha \tau_1 k_a + \beta \Phi_{isc} \quad (10)$$

Φ_1^0 , Φ_3^0 and Φ^0 are singlet, triplet and total quantum yields in the absence of azulene, respectively. In general, the triplet lifetime, τ_3 is greater than the singlet lifetime, τ_1 and T^1 is less efficiently quenched than T^3 .

$$\Phi_1 = \Phi_1^0 \quad (11)$$

$$\Phi_3 = \frac{\beta k_{isc}}{(k_d + k_q[Az]) + (k_d + k_{isc})} - \Phi_{isc} \left(\frac{\beta k_{isc}}{1/\tau_3 + k_q[Az]} \right) \quad (12)$$

$$\Phi_{t,c} = \Phi_1 + \Phi_3 = \Phi_1^0 + \Phi_{isc} \left(\frac{\beta k_{isc}}{1/\tau_3 + k_q[Az]} \right) \quad (13)$$

$$\Phi_3^0/\Phi_3 = \frac{\Phi^0 - \Phi_1^0}{\Phi - \Phi_1^0} = 1 + k_q \tau_3 [Az] \quad (14)$$

$$\Phi^0/\Phi = 1 + \frac{k_q \tau_3 [Az]}{1 + \Phi_1^0/\Phi_1^0 (1 + k_q \tau_3 [Az])} \quad (15)$$

A Stern-Volmer plot as expressed in eq. 15 is not linear but a downward curve²³ in agreement with the experimental data. Subtraction of singlet quantum yield (Φ_1^0) from the total quantum yield at any azulene concentration provides the quantum yield from the triplet excited state and a Stern-Volmer plot for the triplet reaction as expressed in eq. 14 should be linear with a slope equal to $k_q \tau_3$.

The value of ω (i.e., Φ_1^0) was obtained from the linear plot of $(\Phi^0 - \omega)/(\Phi - \omega)$ vs. $[Az]$ according to the procedure reported (eq. 16) by Wagner.²³

$$\frac{\Phi^0 - \omega}{\Phi - \omega} = 1 + \frac{k_q \tau_3 [Az]}{\left(\frac{\Phi^0 - \omega}{\Phi_3^0} \right) (1 + k_q \tau_3 [Az])} \quad (16)$$

Values of ω smaller than Φ_1^0 result in a plot which is still curved downward: ω larger than Φ_1^0 produces a plot which curved upward. It is obvious that eq. 16 collapses into eq. 14 when ω equals to Φ_1^0 .

According to the above procedure, the value of ω (i.e., Φ_1^0) was determined to be 0.14. Using eq. 10 and the value of Φ^0 (= 0.26 in Table 1), Φ_3^0 is calculated to be 0.12.

The calculated values according to eq. 14 is shown in the fourth and last column of Table 1 and their Stern-Volmer plot is shown in Figure 2 which gives $k_q \tau_3$ value of 357 M^{-1} . Since k_q should be equal to diffusion controlled rate constant (about $5.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ in ethanol solution),²⁹ τ_3 is estimated to be $6.5 \times 10^{-8} \text{ s}$.

Sensitized Photostationary State. Extensive studies have established that *cis-trans* photoisomerization of olefins can be triplet sensitized.²⁴ The simplest mechanism under this condition is shown in eq's 17-22 where S stands for the sensitizer.

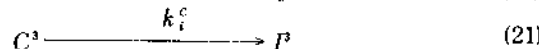
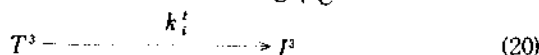
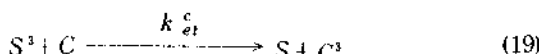
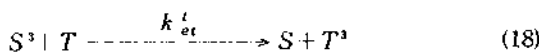
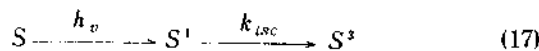
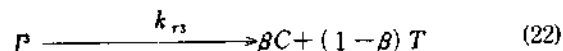


Table 2. External Heavy Atom effect on the *trans-cis* Photoisomerization of I at 366 nm in Ethanol Solution^a

[EtI], M	Φ_{t-c}
0.00	0.26
0.10	0.36
0.20	0.44
0.40	0.45
0.80	0.45

^aConcentration of I is 7.4×10^{-4} M; All photoisomerization reaction is carried out at room temperature and all data are corrected for thermal isomerization reactions.²⁷



In the absence of back-energy transfer from tolrestat triplets to either the sensitizer or some other acceptor, the photostationary composition is determined by k_{et}^i/k_{et}^c , the excitation ratio, and $\beta/1-\beta$, the decay ratio.

$$\left(\frac{T}{C}\right)_{\text{pss}} = \frac{1-\beta}{\beta} \times \frac{k_{et}^c}{k_{et}^i} \quad (23)$$

Triplet sensitizer with sufficiently high triplet energy transfer triplet excitation with equal efficiency to T and C, $k_{et}^i = k_{et}^c = k_{\text{diff}}$.³⁰ For such sensitizers, photostationary state ratios equals the triplet decay ratio.

$$\left(\frac{T}{C}\right)_{\text{pss}} = \frac{1-\beta}{\beta} \quad (24)$$

Xanthone ($E_t = 74$ kcal/mol)²⁹ is used as a triplet sensitizer. The ratio of *cis* to *trans* at photostationary state was about one (1 ± 0.03), hence the value of β is determined to be 0.5. Intersystem crossing quantum yield is calculated to be 0.24 from eq. 9 and internal conversion quantum yield (Φ_{ic}) should be 0.62. The value of α (0.2) can be calculated from the relationship, $\alpha/1-\alpha = \Phi_{ic}^0/\Phi_{ic}$ ($=0.14/0.62$).

External Heavy Atom Effect. Heavy atom enhances the intersystem crossing rate through the increase of spin-orbit coupling and thus affect the reaction quantum yield.³⁴ To get better insight into the reaction mechanism suggested (eq's 1 through 6), the external heavy atom effect was examined using ethyl iodide as heavy atom source in ethanol. If the heavy atom is added to the reaction system, eq. 25 should be added to the mechanistic scheme and eq's 11, 12, and 13 are replaced by eq's 26, 27, and 28, respectively.



$$\Phi_1 = \frac{\alpha k_{it}}{k_{isc} + k_{it} + k_{so}(EtI)} \quad (26)$$

$$\Phi_3 = \frac{\beta(k_{isc} + k_{so}(EtI))}{k_{isc} + k_{it} + k_{so}(EtI)} \quad (27)$$

$$\begin{aligned} \Phi_{t-c} &= \Phi_1 + \Phi_3 \\ &= \frac{1}{k_{isc} + k_{it} + k_{so}(EtI)} (\alpha k_{it} + \beta(k_{isc} + k_{so}(EtI))) \quad (28) \end{aligned}$$

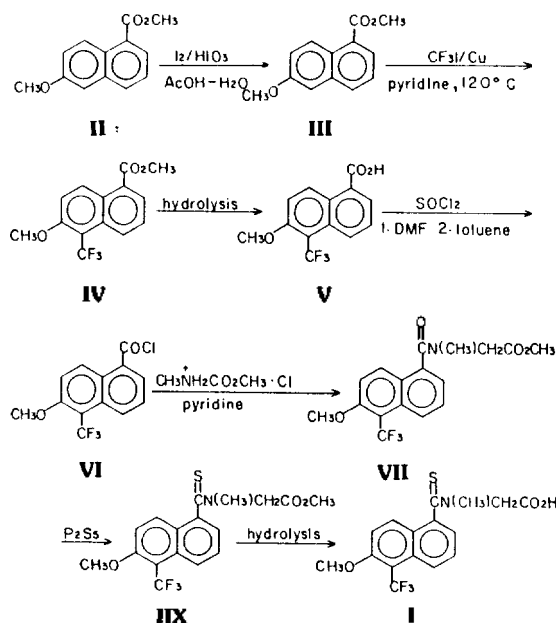
The first and second term of eq. 28 express the contribution of singlet and triplet excited state to the total quantum

yield of photoisomerization of I, respectively. This equation shows that the first term will decrease while the second term increase by increasing the concentration of ethyl iodide. Therefore, increase or decrease of the total quantum yield in the presence of heavy atom is determined by the value of α and β . If the value of β is smaller than α , the total quantum yield will be decreased. If the value of β is equal to α , the total quantum yield will remain the same. If the value of β is larger than α , the total quantum yield will increase. As shown in Table 2, the total quantum yield is increased in the presence of ethyl iodide indicating that the photoisomerization from triplet excited state (β) is more efficient than that from the singlet excited state (α). If the photoisomerization reaction proceeds *via* only triplet excited state ($\Phi_{isc} = 1$), the total quantum yield must be 0.5 ($\Phi = \beta\Phi_{isc}$). As shown in Table 2, the experimentally measurable maximum quantum yield (0.45),²⁷ approaches to this value *i.e.* the data obtained from this experiment is in good agreement with those calculated from the proposed mechanism. The results from two independent experiments support the proposed mechanism.

Experimental

Spectroscopic Measurements. Ultraviolet-visible spectra were recorded on a Cary 17 spectrometer. Proton NMR spectra were recorded on a Bruker model WH-400 NMR spectrometer or Varian FT-80A spectrometer. Infrared spectra were recorded in nujol on a Perkin-Elmer 283B spectrophotometer. Emission spectra were recorded on a Aminco-Bowman spectrophotofluorometer with an Aminco-XY recorder at room temperature and at 77 K with modification of cell compartment. A cylindrical chopper having the maximum rotating frequency of 10,000 rpm with two window opposite to each other was used to isolate phosphorescence from other emission.

Materials. The title compound I was prepared by



Scheme 1. Preparation of N-5-Trifluoromethyl-6-methoxy-1-thionaphthyl-N-methylglycine (Compound I)

methods described elsewhere^{1,2} (Scheme 1). Azulene (Aldrich Chemical Company) was purified by vacuum sublimation and xanthone (Sigma Chemical Company) was recrystallized from ethanol and dried at 100°C. Ethyl iodide (Junsei Chemical Company) was purified by removing free iodine following the procedure reported previously.²⁶ Trifluoromethyl iodide (Aldrich Chem. Co.), HIO₃ (Aldrich Chem. Co.), thionyl chloride (Aldrich Chem. Co.), phosphorus pentasulfide (Aldrich Chem. Co.), N-methylglycine (Aldrich Chem. Co.) and copper powder (Aldrich Chem. Co.) were used without further purification. Chromatographic and spectroscopic grade solvents (Merck) were used for HPLC and absorption and emission spectra, respectively. Doubly distilled and deionized water was also used for HPLC.

6-Methoxy-5-trifluoromethylnaphthoic Acid (V). The key intermediate V, as its methyl ester, was obtained in 87% yield *via* the iodination of methyl-6-methoxy-1-naphthalene carboxylate (II)³⁸ with I₂/HIO₃ in acetic acid-sulfuric acid mixture. The iodo derivative III, mp 98-99°C, was reacted with trifluoromethyl iodide and copper powder in pyridine in an autoclave at 120°C for 20 hr to give IV, mp 75-78°C in 93% yield. Hydrolysis of IV afforded the key intermediate V, mp 221-222°C. ¹NMR (DMSO-d₆) δ 4.0 (s, 3H), 8.3 (m, 5H), 10.6 (broad, 1H).

N-[[Methoxy-5-(trifluoromethyl)-1-naphthoyl] carbonyl]-N-methylglycine Methyl Ester (VII). A catalytic amount (5 drops) of dry dimethyl formamide was added to a suspension of 6-methoxy-5-trifluoromethyl-1-naphthoic acid (9 g, 32 mmol) in thionyl chloride (100 ml). The suspension was heated cautiously to reflux (caution; a vigorous reaction can occur) for 20 min. The mixture was evaporated to dryness. The residue was dissolved in pyridine (100 ml). The solution was cooled in an ice bath. Dry N-methylglycine methyl ester hydrochloride (11.1 g) was added portion-wise to the cooled solution. The mixture was extracted with ethyl acetate (3 × 150 ml) and the combined extracts were washed successively with 1 N aqueous HCl, a saturated aqueous solution of NaHCO₃ and brine. After drying over MgSO₄, the extract was treated with charcoal, filtered and evaporated under reduced pressure to give 7.4 g of the title compound as an oil in 93% yield. ¹NMR (CDCl₃) δ 3.00 (s, 3H), 3.75 (s, 3H), 4.00 (s, 3H), 4.35 and 4.5 (d, 2H), 7.0-8.5 (m, 5H).

N-[[6-methoxy-5-(trifluoromethyl)-1-naphthalenyl] thioxomethyl]-N-methylglycine Methyl Ester (IIX). N-[[6-Methoxy-5-(trifluoromethyl)-1-naphthalenyl] carbonyl]-N-methylglycine methyl ester (VII, 2.0 g, 5.6 mmoles) was dissolved in dry pyridine (40 ml). Phosphorus pentasulfide (2.37 g) was added to the pyridine solution. The mixture was heated at refluxed for 4 hr and then poured into warm water at 50°C to 80°C (caution; evolution of copious quantities of H₂S). The mixture was extracted with ethyl acetate. The extract was washed successively with 3 N aqueous HCl, water, a saturated water solution of NaHCO₃, water and brine, dried over MgSO₄ and concentrated to dryness. The residue was recrystallized from ethanol-water to give 1.6 g of title compound, mp 121-123°C (yield, 77%). ¹NMR (CDCl₃) δ 3.00 (s, 3H), 3.75 (s, 3H), 4.00 (s, 3H), 4.35 and 4.5 (d, 2H), 7.0-8.5 (m, 5H).

N-6-Methoxy-5-trifluoromethyl-1-thionaphthoyl-N-methylglycine(I). N-[[6-Methoxy-5-(trifluoromethyl)-1-naphthalenyl] thioxomethyl]-N-methyl glycine methyl ester (1.4 g,

Table 3. Details of the Analytical and Preparative HPLC Conditions^a

	Analytical HPLC	Preparative HPLC
Column	-Bondapak C-18 (3.9 × 300 mm)	Zorbax ODS 5 (21.2 × 250 mm)
Solvent	MeOH/H ₂ O (v/v, 100/220)	Acetonitrile/H ₂ O/AcOH (v/v, 498/500/2)
Flow Rate	1 ml/min	9 ml/min
Retention Time	<i>cis</i> -; 5 min <i>trans</i> -; 9 min	<i>cis</i> -; 21 min <i>trans</i> -; 27 min

^aPump; Waters Associates (Model 6000A), UV Detector: Waters Associates (Model 440), Recorder; Houston Instrument (Model 5000-746) for preparative and Varian electronic integrater (Model 4290) for analytical HPLC.

3.7 mmoles) in 2-methoxyethanol (20 ml) was stirred at 20-22°C for 4 hr. Water was added and the cloudy mixture was extracted with ethyl acetate. The aqueous layer was made acidic (pH = 3) with 1 N aqueous HCl and extracted with ethyl acetate. The latter extract was washed successively with water and brine, dried over MgSO₄ and concentrated under reduced pressure. The residue was crystallized from chloroform-hexane to give 687 mg of the title compound (yield, 51%). This consisted of 90% of *trans*- and 10% of *cis*-rotamers. Isolation of pure *trans*-rotamer from the mixture was successfully achieved by a semi-preparative HPLC system. Detailed conditions are given in Table 3. Collection of samples was performed using cooled collection flasks. The samples were then freeze-dried after evaporation of organic solvents. ¹NMR (CDCl₃) δ 3.05 (s, 3H), 3.95 (s, 3H), 4.55 and 5.4 (d, J = 17 Hz, 2H), 7.6 (m, 5H), 9.8 (broad, 1H). IR (CHCl₃), 2900 cm⁻¹, 1720 cm⁻¹. UV (EtOH) λ_{max} (ε) 337 nm (3895), 268 nm (13260), 226 nm (49315).

Measurement of Quantum Yields. Samples of 3 ml solution in Pyrex ampoules were degassed by three cycles of freeze-pump-thaw method with cooling in liquid nitrogen and then sealed. These samples were irradiated in a merry-go-round apparatus with Hanovia 450 W medium pressure mercury arc lamp (Type 679A36). The following filters were used to isolate the mercury emission lines; 313 nm, # 7-54 Corning glass filter and a 0.7 cm path of 0.0025 M K₂CrO₄ in 1% Na₂CO₃ aqueous solution; 366 nm, Corning glass filters # 0-52 and #7-37. Light intensities were measured by ferrioxalate actinometry.²² The quantitative analysis was carried out by HPLC. Detailed conditions are shown in Table 3. Peak area ratios (in percent) of *cis* (retention time, 5 min) and *trans* (retention time, 9 min)-rotamers were computed by an electronic integrator.

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Degradation Reaction of the 90K Superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ in H_2O

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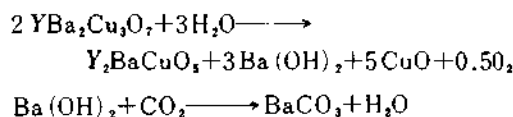
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Degradation of the 90 K superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ in water and humid atmosphere were studied and its decomposition products were identified as BaCO_3 , CuO , $\text{Y}_2(\text{CO}_3)_3 \cdot 3\text{H}_2\text{O}$ and O_2 . XRD analysis, iodometric titration and IR-spectroscopy of the degraded samples suggest that the $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ decomposes in three steps such as the reduction of Cu^{3+} to Cu^{2+} , followed by the hydroxylation of Ba^{2+} and Y^{3+} via hydration and finally the formation of carbonates through the uptake of ambient CO_2 .

Introduction

The reactions of superconducting phase with aqueous media are of interest for several reasons, which include the need of knowledge about material handling in practical application as well as the understanding of degradation mechanism. In recent publications, some of the papers have been dealt with the reaction of the superconducting phase, $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$, with water and it had been gradually understood that the $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ phase decomposes in water to the corresponding metal oxide, carbonates via hydroxides, and oxygen. M.F. Yan *et al.*¹ recently reported that the superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ phase is decomposed by water and water vapor as follows;



B.G. Hyde *et al.*² also observed the bulk decomposition of the superconducting phase $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ in air, whose decomposition products have been identified as $\text{Ba}_2\text{Cu}(\text{OH})_6$, BaCO_3 , CuO and $\text{Y}(\text{OH})_3$. D.C. Harris and T.A. Hewston³ found that the $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ phase is readily soluble in HCl to evolve oxygen gas. F.G. Frase *et al.*⁴ reported the effects of various solvents, including water, on the solubility of the superconducting phase. They observed that water reacts with $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ to form BaCO_3 as the major phase. They