

Photoreaction of 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea in simulated atmosphere

Liu Guoguang*, Jin Zuliang and Xu Xiaobai**

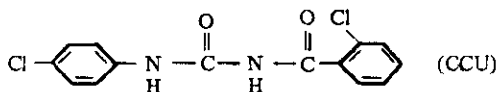
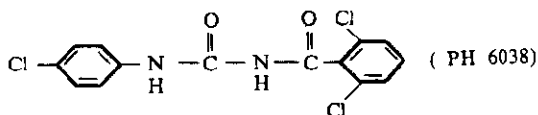
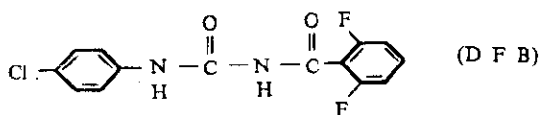
Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Abstract. The photoreaction of 1-(2-chlorobenzoyl)-3-(4-chlorophenyl)urea (CCU) in simulated atmosphere was studied. Rate constants and half-lives of this compound in nitrogen, air and oxygen, upon irradiation with Xenon lamp, were determined. Statistical treatment of experimental results indicated that photoreactions in nitrogen and air were of the first order, while that in oxygen was closer to the second order. The main products of photoreaction of this compound were 2-chlorobenzamide, 4-chlorophenyl urea, 4-chloroaniline, and 2-chloro-N-(4-chlorophenyl)benzamide, and the possible pathways of photodecomposition were suggested.

Keywords: 1-(2-chlorobenzoyl)-3-(4-chlorophenyl) urea; photoreaction; products; mechanism.

INTRODUCTION

A new kind of phenylurea insecticides, which disrupt normal moulting and developing processes of insects, has been developed since 1970s. It includes DFB, PH6038 and CCU with their respective molecular structure as follows:



* Recent address: Department of Chemistry, Henan Normal University, Xinxiang, China.

** To whom correspondence should be addressed

Of these insecticides, CCU was synthesized and commercialized in China during 1980s, and now it is used in agriculture and forestry. After application, some of them will be adsorbed by particulates in the air, where photoreaction will take place. Also will occur photoreaction for those deposited on the surface of plant leaves. In order to know the degradation of CCU in the environment, the photoreaction of CCU in simulated atmosphere was studied (Liu, 1990).

EXPERIMENTAL

Reagents

CCU was produced by Tonghua Factory of Insecticides (Jilin Province). After recrystallization with toluene for three times, its purity is about 98%. All solvents: methanol, dichloromethane, and 1,4-dioxane, were from Beijing Chemical Factory and redistilled before use. Silica gel (100–200 meshes) was from Shanghai Wusi Chemical Factory. Three standard compounds, 4-chloroaniline, 4-chlorophenyl urea and 2-chlorobenzamide were supplied by Wuhan Institute of Hydrobiology, Chinese Academy of Sciences.

Instruments

Shimadzu LC-5A HPLC equipped with SPD-1 UV detector; Branson B-32 ultrasonicator; XQ-200w Xenon lamp with XQ150-500 D. C. power from Shanghai Lightening Device Factory; quartz fluidized bed reaction chambers are self-made; Finnigan MAT-4510 GC/MS.

The reaction equipment is shown in Fig.1 (Zhang, 1989).

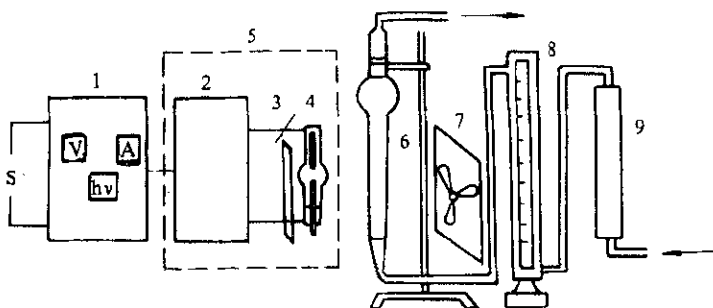


Fig.1 Scheme of fluidized-bed reaction equipment

1. D.C. power supply 2. Trigger 3. Reflector 4. Xenon lamp 5. Lamp box 6. Fluidized-bed reaction chamber 7. Fan for cooling 8. Flowmeter 9. Carrier gas purifier

Experimental method (Liu, 1990)

1. HPLC analysis (Rossum, 1983; Opdycke, 1982; Chiavari, 1985)

HPLC was used to determine the concentration of CCU during the process of experiment. The chromatographic conditions were. HPLC column: 250 × 4.6 mm, filled with 5 μm Lichrosorb

RP-18, mobile phase: $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ (90:10, v/v), at flow rate 1 ml/min, detection wavelength: UV-254nm.

2. Preparation of photoreaction sample

Silica gel (100–200 meshes) was selected as the carrier. It was firstly extracted three times with methanol in ultrasonicator, then extracted 20 hours in soxhlet extractor with dichloromethane for purification. After evaporating off the solvent and drying at 110°C , the silica gel was kept in desiccator before use.

The weighed CCU sample was dissolved in dichloromethane, and the solution was poured in several times to a definite amount of silica gel in an Erlenmeyer flask. The solution quantity for each time was just enough to cover the silica gel. Then the silica gel was dried at 40°C , and transferred it into desiccator for use. The residue of CCU in the flask was dissolved with dioxane, and its concentration was determined. The amount of CCU on silica gel was calculated as follows

$$\text{CCU on silica gel, (mg/g)} = \frac{\text{Total amount of CCU} - \text{Residue of CCU in flask}}{\text{Weight of silica gel}}$$

Five aliquot samples were taken in parallel. After extracting with methanol, the maximum relative deviation of the CCU amount of each sample determined is below 1.2%. This result shows that the sample is comparatively uniform.

3. Exposure experiment

About 1 g sample was introduced into the reaction chamber (Fig.1) each time. Nitrogen, air or oxygen was used as carrier gas, respectively, with the flow rate controlled at 100 ml/min for keeping the sample in fluidized condition. The reaction temperature was kept at $25 \pm 2^\circ\text{C}$ during exposure under Xenon lamp. A certain amount of silica gel in the chamber was sampled for every fixed time interval. The variation of concentration of CCU on silica gel with exposure, after extracting with dioxane and analyzing with HPLC was studied.

Meantime, parallel experiments were carried out in the dark for comparison.

4. Identification of the photoproducts

The sample after exposure for 120 hours was taken out from reaction chamber, and extracted with methanol. The extract was concentrated to 1 ml, and then the products were identified as follows:

(1) Separation and identification by HPLC

The chromatographic conditions used were: HPLC column: $250 \times 4.6\text{mm}$, Zorbax C_8 ; mobile phase: $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ (70:30, v/v), flow rate: 0.4 ml/min; detector: UV-254 nm.

(2) Identification with GC-MS and MS

GC/MS: GC system, SE54 capillary silica column of $30\text{m} \times \text{i.d.} 0.22\text{ mm}$, column temperature programming from 60 to 220°C at $4^\circ\text{C}/\text{min}$, from 220 to 300°C at $10^\circ\text{C}/\text{min}$; MS system, electron impact mode at 70 eV , ion current at $270\ \mu\text{A}$, mass scan range: $33-500\text{ amu}$, with scan

speed at 30 /min, ionization temperature: 300°C.

Direct probe MS: ionization temperature increases from 80 to 300°C at 30°C/min.

RESULTS AND DISCUSSION

Photoreaction kinetics

The photoreaction results of CCU in nitrogen, air and oxygen are shown in Fig.2.

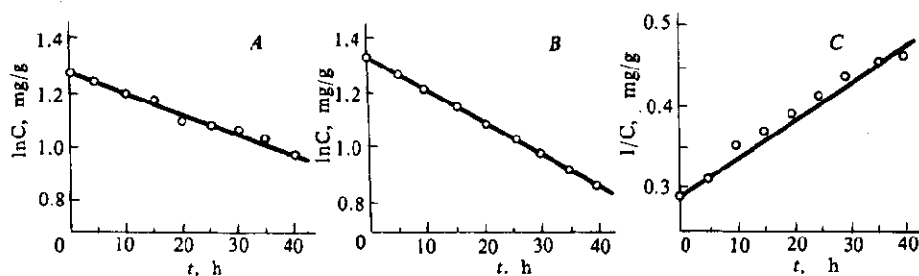


Fig.2 Photoreaction kinetic curves of CCU in various carrier gases

A: nitrogen B: air C: oxygen

When the photoreaction was carried out in nitrogen or air, the $\ln c$ kept linear with t . This showed that both of the photoreactions were of the first order. When the photoreaction occurred in oxygen, $1/c$ kept linear with t , showing that the reaction was more of the second order. The photoreaction equations are:

$$\text{under nitrogen} \quad \ln 1/c = -1.27 + 0.00703 t \quad r=0.989$$

$$\text{under air} \quad \ln 1/c = -1.32 + 0.0109 t \quad r=0.997$$

$$\text{under oxygen} \quad \ln 1/c = 0.295 + 0.00445 t \quad r=0.983$$

Here, t is photoreaction time (h), c is concentration of CCU at time t (mg/g), r is correlation coefficient.

The half-lives of CCU in these three carrier gases are $t_{1/2}(\text{N}_2) = 98.6\text{h}$, $t_{1/2}(\text{air}) = 63.6\text{h}$, $t_{1/2}(\text{O}_2) = 62.7\text{h}$, respectively.

Meanwhile, CCU reaction under dark condition was very slow, so the dark reaction was ignored.

Photoreaction products

1. Identification with HPLC

The chromatograms of photoproducts of CCU in nitrogen, air and oxygen are shown in Fig. 3.

Fig. 3 shows that the main photoproducts of CCU in three gaseous media are almost the same, only that there is a minor difference for the products in nitrogen. Comparing with the HPLC chromatograms of standard compounds, we found that the retention times relative to peak 1, 2 and 3 were equal to those of 2-chlorobenzamide, 4-chlorophenyl urea and

4-chloroaniline, respectively. The UV absorption spectra of peak 1,2 and 3 in Fig.3 and those of the relative standard compounds are also recorded and are compared in Fig.4.

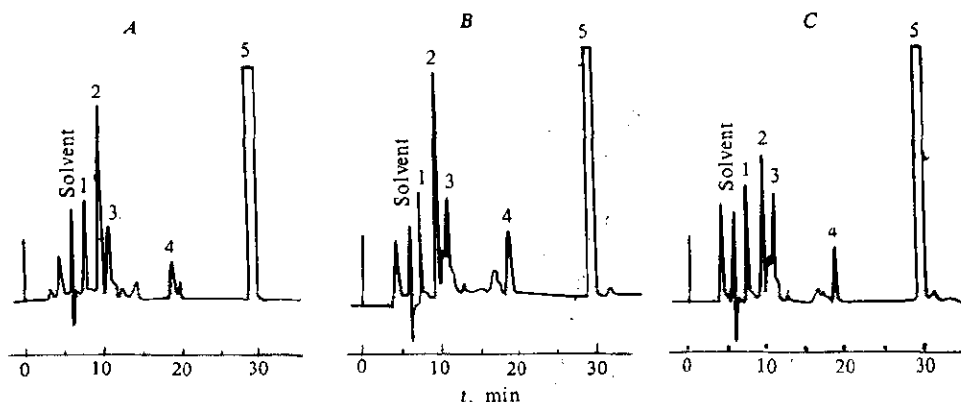


Fig.3 HPLC chromatograms of photoreaction products of CCU in various carrier gases

A: nitrogen B: air C: oxygen

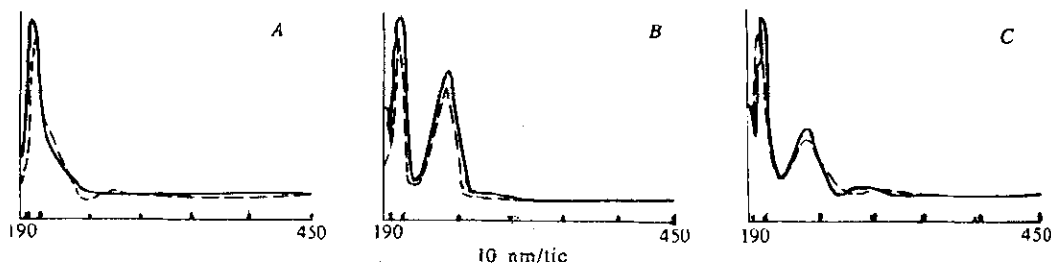


Fig.4 UV absorption spectra of photoproducts in comparison with those of standards (taken from HP 1090 HPLC, ---photoproducts, ---standards)

A: peak 1,2-chlorobenzamide B: peak 2, 4-chlorophenyl urea C: peak 3,4-chloroaniline

Fig.4 shows that UV spectra of each pair are very similar. Thus, peak 1, 2 and 3 in Fig.3 were identified respectively as 2-chlorobenzamide, 4-chlorophenyl urea and 4-chloroaniline both from their retention times as well as from their UV spectra.

2. Identification with off-line HPLC/MS

The eluting fractions collected from the preparative HPLC column were identified with direct probe MS. Mass Spectra of peak 2,4 and 5 shown in Fig. 5 were identified as 4-chlorophenyl urea, 2-chloro-N-(4-chlorophenyl)-benzamide, and CCU.

3. Identification with GC-MS

Both the photoproducts of CCU in nitrogen and oxygen were also studied using GC-MS. The results expressed that there were 4-chlorophenyl isocyanate, 2-chlorobenzamide, 4-chloroaniline, 2-chlorobenzoyl hydrazine, and 2-chloro-N-(4-chlorophenyl) benzamide in both

conditions. Meanwhile, an unidentified photoproduct with molecular weight 121 was found in oxygen. The representative mass spectra of photoproducts in oxygen are as in Fig. 6, while those in nitrogen are mainly the same (not shown).

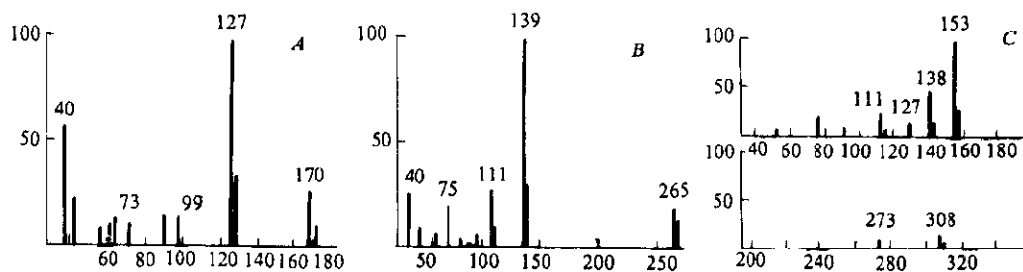


Fig. 5 Mass spectra of HPLC fractions of peaks in Fig. 3.

A: peak 2 B: peak 4 C: peak 5

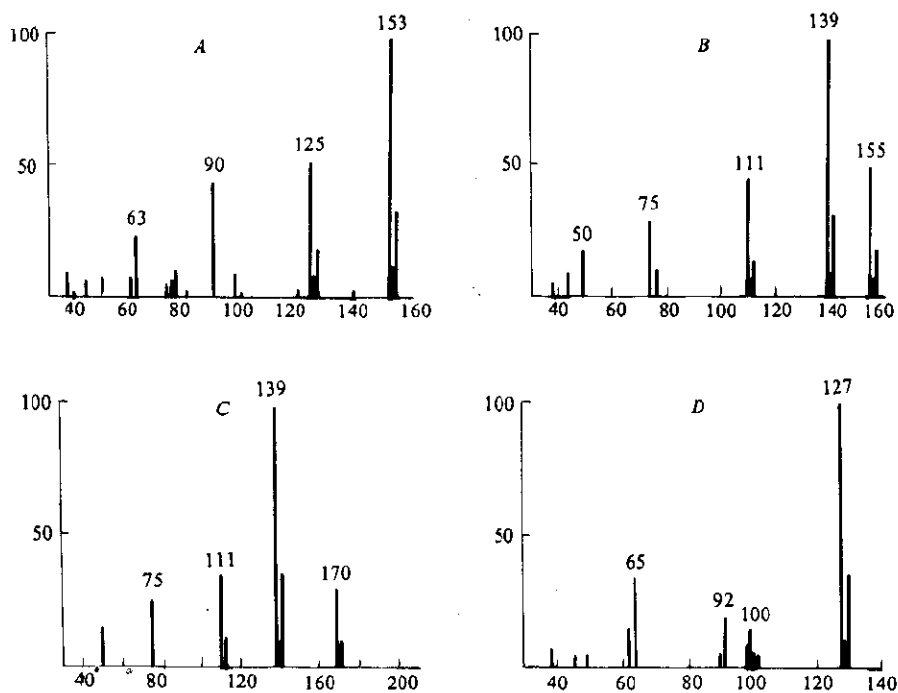


Fig. 6 Mass spectra of photoproducts from GC-MS

A: product a B: product b C: product d D: product e

4. Main photoproducts

All the products of CCU identified with HPLC-UV, off-line HPLC-MS, and GC-MS are

summarized in Table 1. However, at this stage we do not have all these chemicals available as standards for quantitation.

Table 1 Main photoreaction products of CCU in simulated atmosphere

Product No.	Peak No. in HPLC	RT(HPLC), min	RT(GC-MS), min	Mol. wt.	Main MS fragm.	Formula
a	—	—	15.8	153	155, 125, 90	C ₆ H ₄ ClNO
b	1	7.5	27.8	155	157, 139, 111	C ₇ H ₆ ClNO
c	2	9.8	—	170	172, 127	C ₇ H ₆ Cl ₂ O
d	3	11.0	18.4	127	129, 92	C ₆ H ₅ ClN
e	—	—	20.8	170	172, 139, 111	C ₇ H ₆ Cl ₂ O
f	4	18.8	47.7	265	267, 139, 111	C ₁₀ H ₈ Cl ₂ NO
g	5	30.0	—	308	310, 153, 139 127, 111	C ₁₀ H ₈ Cl ₂ N ₂ O ₂

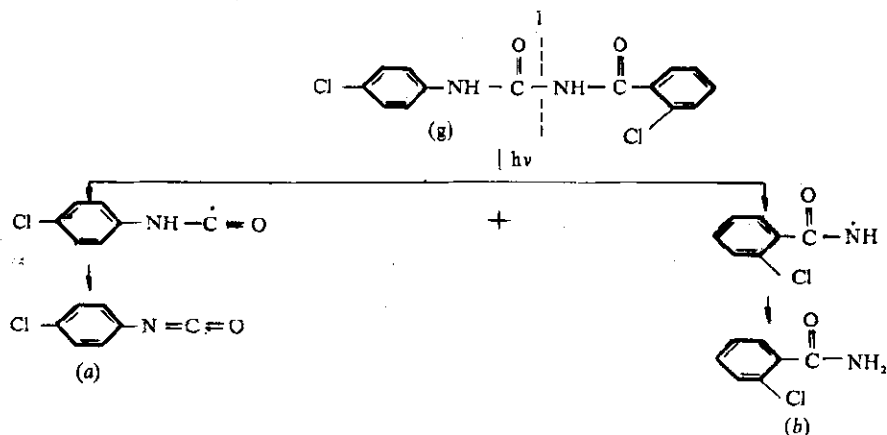
a. 4-chlorophenyl isocyanate³ b. 2-chloro benzamide^{1,3} c. 4-chlorophenyl urea^{1,2} d. 4-chloroaniline^{1,3}
 e. 2-chlorobenzoyl hydrazine³ f. 2-chloro-N-(4-chlorophenyl)^{2,3} benzamide g. CCU^{1,2} ¹HPLC-UV ²HPLC/MS
³GC-MS (tentative identification)

In order to assure the identity of the most abundant product, the relative absorption UV-254 of the standard solutions was determined. The relative absorption of 4-chlorophenyl urea, 4-chloroaniline, and 2-chlorobenzamide were determined is found to be 24:19:1. Thus although on the HPLC chromatogram (Fig. 3), peak 2 (corresponding to the 4-chlorophenyl urea) is higher than peak 1 (corresponding to the 2-chlorobenzamide) still the latter seems to be larger in quantity. This happens to be consistent with the relative peak height of TIC chromatograms from GC-MS. So 2-chlorobenzamide was confirmed as the most important photoproduct.

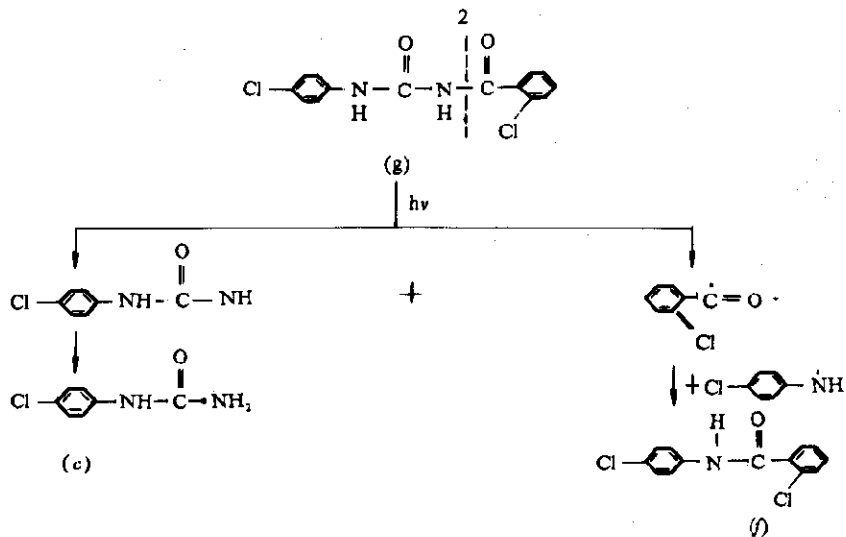
Proposed mechanism of photoreaction

From the photoproducts in Table 1, we suggest that the possible photoreaction pathways of CCU might be as follows:

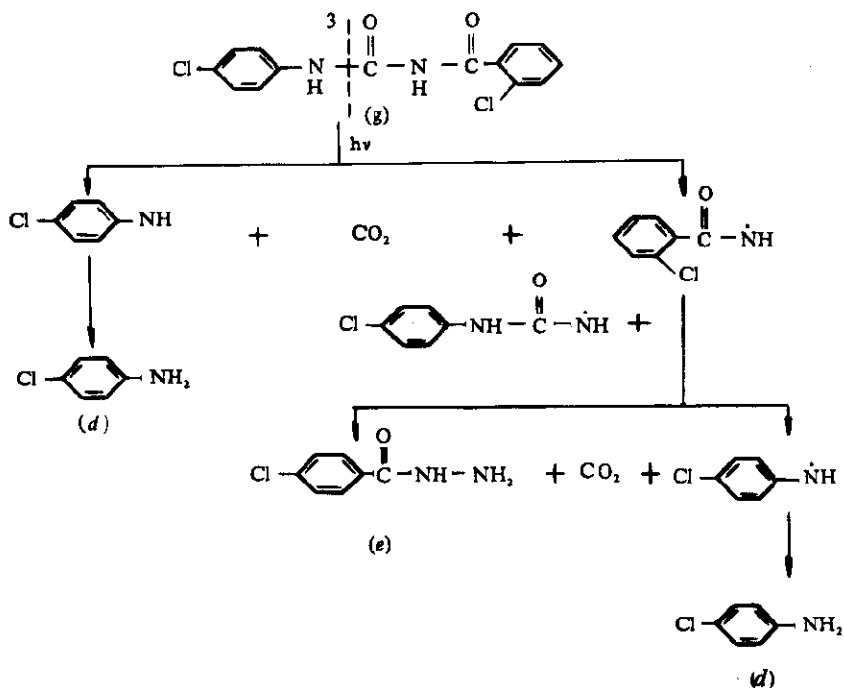
Pathway 1



Pathway 2



Pathway 3



As 2-chlorobenzamide is the most abundant product, the pathway 1 is proposed as the main one.

CONCLUSIONS

1. The photoreaction of CCU can take place in all the three carrier gases. Both reactions in nitrogen and air are the first order, while that in oxygen is closer to that of second order. The half-lives of CCU in nitrogen, air and oxygen are 98.6, 63.6 and 62.7 hours, respectively.

2. The main photoproducts of CCU in simulated atmosphere are 2-chlorobenzamide, 4-chloroaniline, 4-chlorophenyl urea, and 2-chloro-N-(4-chlorophenyl) benzamide and so on.

3. The photoreaction of CCU in simulated atmosphere might be through the free radical degradation pathway. Under the light irradiation, the amide bond #1 of the CCU molecule most likely breaks up the first, then rearrangement or recombination occurs to form products. Other amide bonds (#2, #3) also might break up but to lesser degree.

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