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THE HYDROLYTIC STABILITY OF SOME CYCLOUREA COMPOUNDS

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Abstract

The hydrolytic behavior of some cyclourea compounds was studied in a Calvet microcalorimeter and a hydrolytic testing apparatus. Information was obtained on their hydrolytic stabilities.

Keywords: cyclourea compounds, cyclourea nitramines, hydrolytic stability, microcalorimetry

Introduction

Hydrolytic stability is one of the most important aspects of cyclourea compounds. There are a few reports on study of the hydrolytic behavior of these compounds, such as their kinetics [1] and mechanisms [2, 3]. The relationship between the hydrolytic stability and the electronic structure of this kind of compound has also been studied in one paper [4]. However, determination of the hydrolytic stabilities of cyclourea compounds by the use of microcalorimetry has not yet been reported. The aim of this work was to study the hydrolytic behavior of some cyclourea compounds with a microcalorimeter and a hydrolytic testing apparatus, and to discuss the influence of the substituents on the nitrogen atoms adjacent to the carbonyl group in the cyclourea compounds on their hydrolytic stabilities.

Experimental

Materials

The following 22 cyclourea compounds were prepared and purified in our institute and were used in this work:

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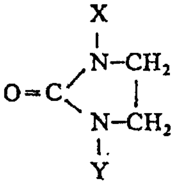
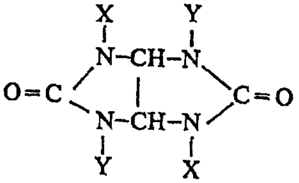
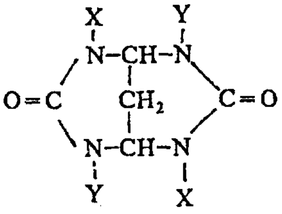


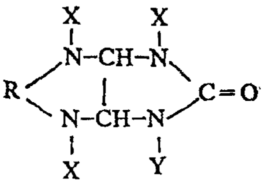
$X=Y=H$, I
$X=Y=CH_2OH$, II
$X=Y=CH_2C(NO_2)_3$, III
$X=NO_2$, $Y=CH_2C(NO_2)_3$, IV
$X=Y=NO_2$, V



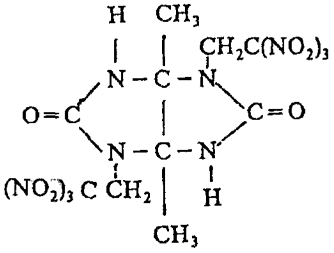
$X=Y=H$, VI
$X=H$, $Y=CH_2OH$, VII
$X=Y=CH_2OH$, VIII
$X=H$, $Y=CH_2C(NO_2)_3$, IX
$X=H$, $Y=NO_2$, X
$X=NO_2$, $Y=CH_2C(NO_2)_3$, XI
$X=Y=NO_2$, XII



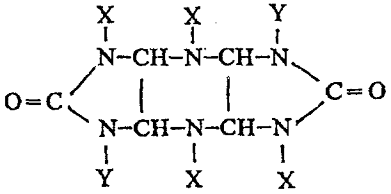
$X=Y=NO_2$, XIII
$X=CH_2C(NO_2)_3$, $Y=NO_2$, XIV



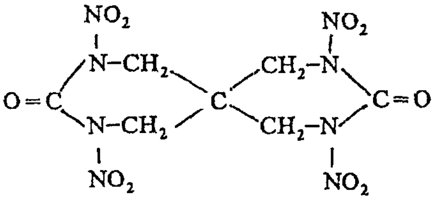
$X=Y=NO_2$, $R=CH_2$, XV
$X=Y=NO_2$, $R=(CH_2)_2$, XVI
$X=NO_2$, $Y=H$, $R=CH_2$, XVII
$X=NO_2$, $Y=CH_2C(NO_2)_3$,
$R=(CH_2)_2$, XVIII



XIX



$X=Y=NO_2$, XX
$X=OH$, $Y=NO_2$, XXI



XXII

The structures of compounds I–XXII were characterized by elemental analyses, molecular weight measurements, IR spectrometry, mass spectrometry and nuclear magnetic resonance spectrometry. Their purities were more than 99.0%. The compounds were kept in a vacuum desiccator before use.

Experimental equipment and conditions

The heat flow curves of the hydroscopic and hydrolytic processes of cyclourea compounds were measured with a Calvet microcalorimeter, type E (SETARAM, France), which had a sensitivity of 66.5 μV mW^{-1} and was equipped with two 15 ml vessels. The microcalorimeter was calibrated via the Joule effect. The heat precision of the enthalpy measurements was 2%. The heat flow of hydroscopic and hydrolytic processes of cyclourea compounds with masses of about 50 mg were measured constantly under conditions of 96% RH and 95°C. The device used is shown in Fig. 1.

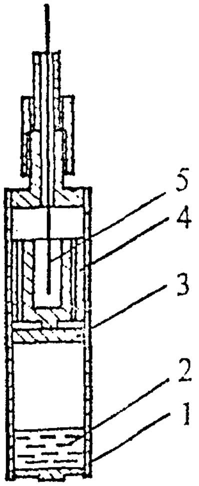


Fig. 1 Device used for study of hydroscopic and hydrolytic processes. (1) Calorimetric cell; (2) saturated solution of K_2SO_4; (3) baffle plate; (4) adding cell containing cyclourea compound; (5) glass rod (on depression of the rod, the baffle plate is dropped into the saturated solution, which makes water vapor with 96% RH pass into the sample space)

The hydrolytic rate constants of some cyclourea nitramines were obtained from an isothermal curve of mass loss *vs.* time with a hydrolytic testing apparatus [5]. The characteristic infrared absorption frequency of the carbonyl group in the cyclourea compounds was obtained with a 60 SXR FT-IR (Nicolet Co., USA).

Results and discussion

The structure parameters [Taft's constant (δ) of the substituents and the infrared absorption frequency of C=O, ($\nu_{C=O}$)] for compounds I–XII, and the hydrolytic rate constants (*k*) for compounds III–V and IX–XII, are shown in Table 1. Typical heat flow curves of compounds III, V, VIII, XII, XIII, XV–XVII and XIX–XXII depicted in Figs 2 and 3.

Table 1 Data on the structural parameters and hydrolytic rate constants (*k*) of some cyclourea compounds

Comp.	Substituents		Structural parameters				$k\cdot10^8$ mol day^{-1}	
	X	Y	Taft's constant			$\gamma^{*}_{C=O}$ cm^{-1}	35°C	45°C
			δ_x	δ_y	$\Sigma\delta_{x,y}$			
I	H	H	0.49	0.49	0.98	1680		
II	CH_2OH	CH_2OH	0.555	0.555	1.11	1695		
III	$CH_2C(NO_2)_3$	$CH_2C(NO_2)_3$	1.62	1.62	3.24	1730	4.6	
IV	NO_2	$CH_2C(NO_2)_3$	3.92	1.62	5.54	1765	12	
V	NO_2	NO_2	3.92	3.92	7.84	1800	24	
VI	H	H	0.49	0.49	0.98	1700		
VII	H	CH_2OH	0.49	0.555	1.045	1720		
VIII	CH_2OH	CH_2OH	0.555	0.555	1.11	1730		
IX	H	$CH_2C(NO_2)_3$	0.49	1.62	2.11	1740		12
X	H	NO_2	0.49	3.92	4.41	1785		87
XI	NO_2	$CH_2C(NO_2)_3$	3.92	1.62	5.54	1805		0.76
XII	NO_2	NO_2	3.92	3.92	7.84	1825		20800

*Characteristic IR absorption frequency of carbonyl group.

From Table 1 and Figs 1 and 2, the following observations may be made:

1. For compound VIII, one endothermic peak corresponding to the hydroscopic process is obtained, whereas the others each give one exothermic peak corresponding to the hydrolytic process.
2. The substitution of two nitro groups for two trinitroethyl groups on the nitrogen atoms adjacent to the carbonyl group (compare V with III) decreases the hydrolytic stability.
3. The substitution of two trinitroethyl groups for two nitro groups on the nitrogen atoms adjacent to the carbonyl groups (compare IX with X, and XI with XII) increases the hydrolytic stability.

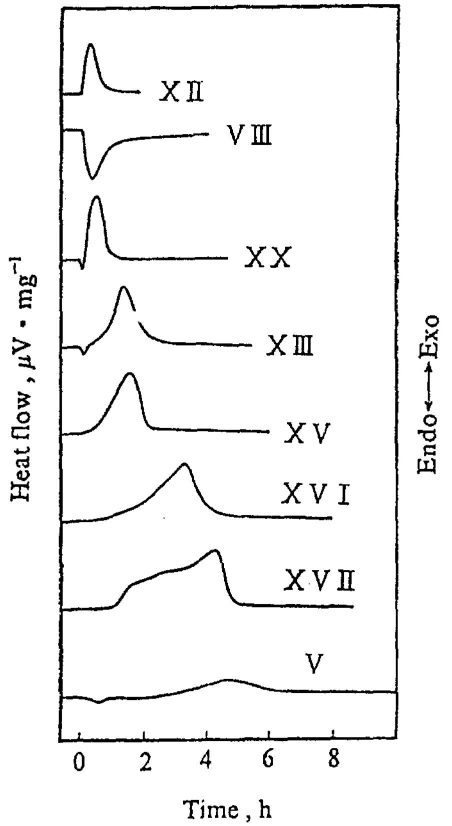


Fig. 2 Heat flow curves of cyclourea compounds V, VIII, XII, XV–XVII and XX under conditions of 96% RH and 95°C

4. The replacement of methyl by ethyl increases the hydrolytic stability (compare XVI with XV).

5. The methylation of XII increases the hydrolytic stability (compare XIII with XII).

6. The hydrolytic stability of XV is lower than that of XVII. This indicates that the substitution of one hydrogen atom for one nitro group on the nitrogen atom adjacent to the carbonyl group can increase the hydrolytic stability.

7. The effect of ring incorporation decreases the hydrolytic stability (compare XII with V).

8. On increase of the value of $\nu_{C=O}$, the hydrolytic stabilities of the cyclourea compounds decrease.

9. The relationship between the characteristic IR absorption frequency of the carbonyl group ($\nu_{C=O}$) and the summation of Taft's constants of the substi-

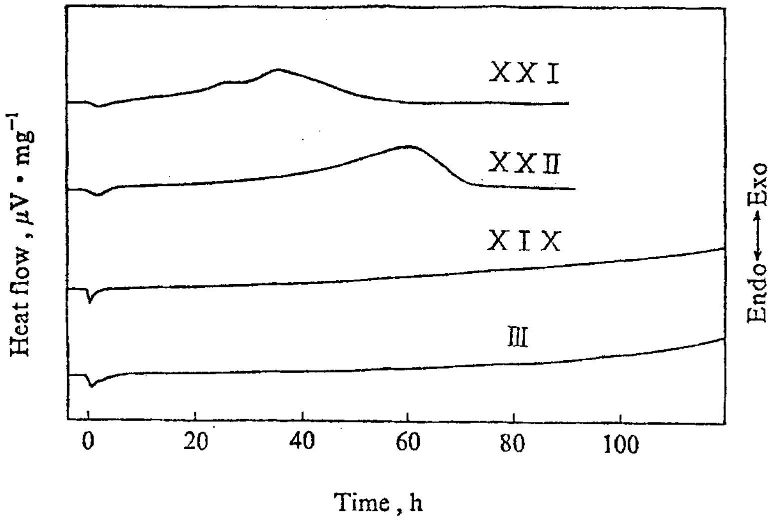


Fig. 3 Heat flow curves of cycloureа compounds XXI, XXII, XIX and III under conditions of 96% RH and 95°C

tuents on the nitrogen atoms adjacent to the carbonyl group for the cyclourea compounds ($\Sigma\delta_{(x,y)}$) can be expressed by the following equations:
for I–V:

$$\nu_{C=O}=1672+16.65\ \Sigma\delta_{x,y},\ r=0.9942$$

and for VI–XII:

$$\nu_{C=O}=1702+17.05\ \Sigma\delta_{x,y},\ r=0.9740$$

10. The hydrolytic stability of XII is the lowest; its value of k at 45°C is $20800\cdot10^{-8}$ day^{-1}

11. The increase in the hydrolytic stability of cyclourea nitramines after replacement of a nitro group with a trinitroethyl group is related to the following facts. Firstly, $\delta_{NO_2}=3.92$ is greater than $\delta_{CH_2\text{-}C(NO_2)_3}=1.62$. Hence, the induction effect of the nitro group on the carbonyl group is greater than that of the trinitroethyl group on the carbonyl group, and the electron cloud density on the carbon atom of the carbonyl group of cyclourea nitramines with an N-trinitroethyl group is greater than that on the carbon atom of the carbonyl group of cyclourea nitramines with an N-nitro group, which makes it difficult for a nucleophilic agent (water) to react with the carbonyl group. Secondly, the volume (93.69 Å^3) of the trinitroethyl group is greater than that (23.50 Å^3) of the nitro group. The spatial obstruction obviously increases. This spatial effect prevents

water from reacting with the carbonyl group. Thirdly, the conjugated direction of the π-bond formed by C=O with $-NO_2$ is the same as that of the induction effect, whereas there is no conjugated effect in cyclourea nitramines containing a trinitroethyl group, which results in the electron cloud density on the carbon atom of the carbonyl group of cyclourea nitramines containing a trinitroethyl group being greater than that on the carbon atom of the carbonyl group of cyclourea nitramines containing only a nitro group.

In conclusion, the hydrolytic stability of a cyclourea compound is closely related to the substituents on the nitrogen atom adjacent to the carbonyl group.

Compound III is of potential for use as a high explosive from the point of view of its hydrolytic stability.

References

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