

# 硝化棉的热分解机理

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**摘要** 建立了实时测定硝化棉(NC)热分解气相产物和凝聚相产物的快速热裂解原位反应池(气体原位反应池)/快速扫描傅立叶变换红外光谱(RSFT-IR)和固体原位反应池/RSFT-IR联用装置。提出了测定上述产物的两种方法。用上述方法研究了在线性升温条件下NC的热分解反应。根据所得结果,提出了该反应的机理。

**关键词** 快速热裂解原位反应池/RSFT-IR 硝化棉 固体原位反应池/RSFT-IR 热分解 机理

中图法分类号 TQ560.1 O657.3

## 1 引言

硝化棉(NC)是单、双、三基火药和混合炸药的组分之一。高氮量NC(14.14%N)与火、炸药中常用的NC(13.20%N)相比,燃气平均分子量提高5.1%,火药力提高6.4%,定容爆热和爆温提高12.0%,受到国内外火炸药工作者的极大关注。为了推动高氮量(氮量高于13.60%)NC在新型火、炸药中的应用,我们开展了NC的热分解机理和模拟燃烧条件下的快速热裂解行为的研究。这对于NC耐热性的评定和燃烧初始阶段数学模型的建立是有益的。

## 2 文献综述

关于NC的热分解机理,Lurie等人<sup>[1-6]</sup>研究了NC热分解过程中的脱硝机理,认为NC热分解的初始阶段是仲O-NO<sub>2</sub>基脱硝逸出NO<sub>2</sub>的过程。Pfeil等人<sup>[7]</sup>在0.5K·min<sup>-1</sup>的慢速升温条件下考察了NC的硝基吸收强度和平均分子量随温度的变化,证实加热过程中,NC先由大分子变为小分子,尔后才发生O-NO<sub>2</sub>键的断裂。Jutier<sup>[8]</sup>则认为NC的热分解是一个脱硝过程,并不一定导致链节的断裂。Brill等人<sup>[9]</sup>通过快速热裂解原位反应池(气体原位反应池)与快速扫描傅立叶变换红外光谱(RSFT-IR)联用技术,测定了NC在快速升温条件下(140K·s<sup>-1</sup>)分解的气相产物,得到了NO、NO<sub>2</sub>、CO、CO<sub>2</sub>、CH<sub>2</sub>O、HCOOH的相对百分浓度与时间的关系图,认为CH<sub>2</sub>O来自-CH<sub>2</sub>ONO<sub>2</sub>基的分解,HCOOH是凝聚相产物的分解产物。

### 3 实验部分

#### 3.1 试 样

NC(14.14%N)和 NC(13.78%N)由我所应用化学研究部制备和纯化。NC(13.54%N)、NC(12.97%)和 NC(11.92%N)由惠安化工厂提供。

#### 3.2 仪器及实验条件

在非等温条件下,NC 的热分解实验在固体原位反应池/RSFT-IR 联用装置和美国 CDS 公司产气体原位反应池/RSFT-IR 联用装置上进行。固体原位反应池/RSFT-IR 联用装置的操作条件为:试样量,约 0.7mg;试样/KBr,1/100;丙酮溶解、干燥压片;升温速率,20 K·min<sup>-1</sup>;实验在固体原位反应池敞口条件下进行;红外分辨率,4cm<sup>-1</sup>;光谱采集速率,18files·min<sup>-1</sup>,8scans·file<sup>-1</sup>;检测器选用 DTGS 型。气体原位反应池/RSFT-IR 联用装置的操作条件为:试样量,1~2mg,平铺在快速加热的铂丝中央;气氛,高纯氮气;加热速率,50、100 和 140K·s<sup>-1</sup>;裂解气体产物在试样上方几毫米处被快速扫描的 FT-IR 光谱仪检测;红外分辨率,4 或 8cm<sup>-1</sup>;光谱采集速率,5files·s<sup>-1</sup>,2scans·file<sup>-1</sup>;检测器选用 MCT-A 型。

### 4 结果与讨论

等速升温条件下 NC(14.14%N)热分解凝聚相的 IR 谱示于图 1。图中同时给出室温下的 IR 谱,以便比较。室温下 IR 谱中各特征吸收峰的指配列在表 1 中。IR 特征吸收峰相对强度与时间、温度的关系数据见表 2~5。由此可见,在 NC 的热分解过程中,首先发生的是 O-NO<sub>2</sub> 键的断裂。随着温度的升高,-NO<sub>2</sub> 基的特征吸收峰强度逐渐减小,至 463K,-NO<sub>2</sub> 基特征吸收峰消失,在 1749cm<sup>-1</sup>处新出现的 C=O 基的特征吸收峰强度逐渐增强,至 448K 时达最大值。与此同时,1067cm<sup>-1</sup>处的环间 C-O-C 基的特征吸收峰强度逐渐降低;而 NC 环和环内 C-O-C 基的振动吸收峰强度的降低则明显滞后,这说明 NC 分解过程中先由大分子变为小分子,尔后才发生环内碳骨架及氧桥的断裂。随着温度的升高,1381cm<sup>-1</sup>附近的弱峰吸收强度逐渐增强,说明 NC 分解过程中有硝酸根离子产生。该离子可能来自反应 2NO<sub>2</sub> + KBr = KNO<sub>3</sub> + NOBr。产物 NOBr 仅在室温下存在<sup>[10]</sup>,在 393~463K 的温度范围内则分解成 Br<sub>2</sub> 和 NO。

NC(13.78%N)快速热裂解气相产物的 IR 谱示于图 2,各气相产物的 IR 特征吸收峰频率及绝对强度列于表 6 中。IR 特征吸收峰积分值和相应吸收峰的绝对强度<sup>[11]</sup>的比值随时间的变化数据列于表 7~9 中。在升温速率 50K·s<sup>-1</sup>条件下,第一张有气相产物出现的 IR 谱中只有 NO<sub>2</sub> 气体的特征吸收峰(数据见表 7),这表明 NC 分解初始阶段脱硝逸出 NO<sub>2</sub> 气体。这与固体原位反应池/RSFT-IR 联用分析证实 NC 受热过程中 -NO<sub>2</sub> 基强度首先发生降低的事实相符。逸出的 NO<sub>2</sub> 作用于分解凝聚相残余物,使 NO<sub>2</sub> 转化为 NO,同时生成大量碳的氧化物,以 CO 和 CO<sub>2</sub> 形式逸出。HCOOH 的出现滞后于其余气体产物,表明 HCOOH 是凝聚相分解产物的二次反应产物。CH<sub>2</sub>O 是伯 O-NO<sub>2</sub> 基的分解产物。在氮量高的 NC 中,伯 O-NO<sub>2</sub> 基含量相对低于常用 NC,生成的 CH<sub>2</sub>O 相对较少,完全被掩盖在 HCOOH 吸收峰中。

由以上实验事实可知,NC 热分解过程中首先发生仲 O-NO<sub>2</sub> 基的脱硝,形成 C=O 基,放出 NO<sub>2</sub> 气体。伴随脱硝的是 NC 由大分子经环间 C-O-C 的断裂形成小分子,最初逸出的 NO<sub>2</sub> 作用于凝聚相,引发自催化反应,加速剩余 O-NO<sub>2</sub> 键的断裂和环内氧桥的断裂,进一步放出 NO<sub>2</sub>、NO、CO、CO<sub>2</sub>、CH<sub>2</sub>O 等气体。大多数 O-NO<sub>2</sub> 基分解后,剩余凝聚相继续分解,放出 HCOOH 气体。根据固体原位反应池和气体原位反应池与 RSFT-IR 联用技术的分析结果,我们推测 NC 受热分解的机理为:

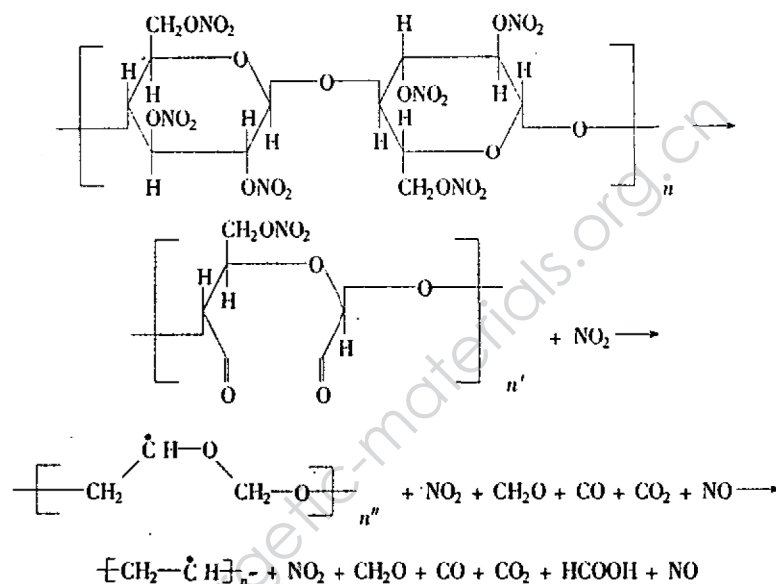


表 1 室温下 NC(14.14%N)的 IR 特征吸收峰的指配

Table 1 Assignments of the IR characteristic absorption peaks of NC (14.14%N) at ambient temp.

| 频率/cm <sup>-1</sup> | 相对强度 | 指 配                       |
|---------------------|------|---------------------------|
| 2966                | 中等   | - CH <sub>2</sub> 不对称伸缩振动 |
| 2927                | 中等   | - CH 伸缩振动                 |
| 1661                | 极强   | - NO <sub>2</sub> 不对称伸缩振动 |
| 1381                | 中等   | - CH 弯曲振动                 |
| 1279                | 极强   | - NO <sub>2</sub> 对称伸缩振动  |
| 1159                | 中等   | 不对称氧桥伸缩振动                 |
| 1116                | 中等   | 不对称环伸缩振动                  |
| 1067                | 极强   | 环间 C-O 伸缩振动               |
| 1022                | 弱    | C-O 伸缩振动                  |
| 1002                | 中等   | C-O 伸缩振动                  |
| 836                 | 极强   | O-NO <sub>2</sub> 伸缩振动    |
| 746                 | 中等   | O-NO <sub>2</sub> 扭曲振动    |
| 688                 | 中等   | O-NO <sub>2</sub> 扭曲振动    |

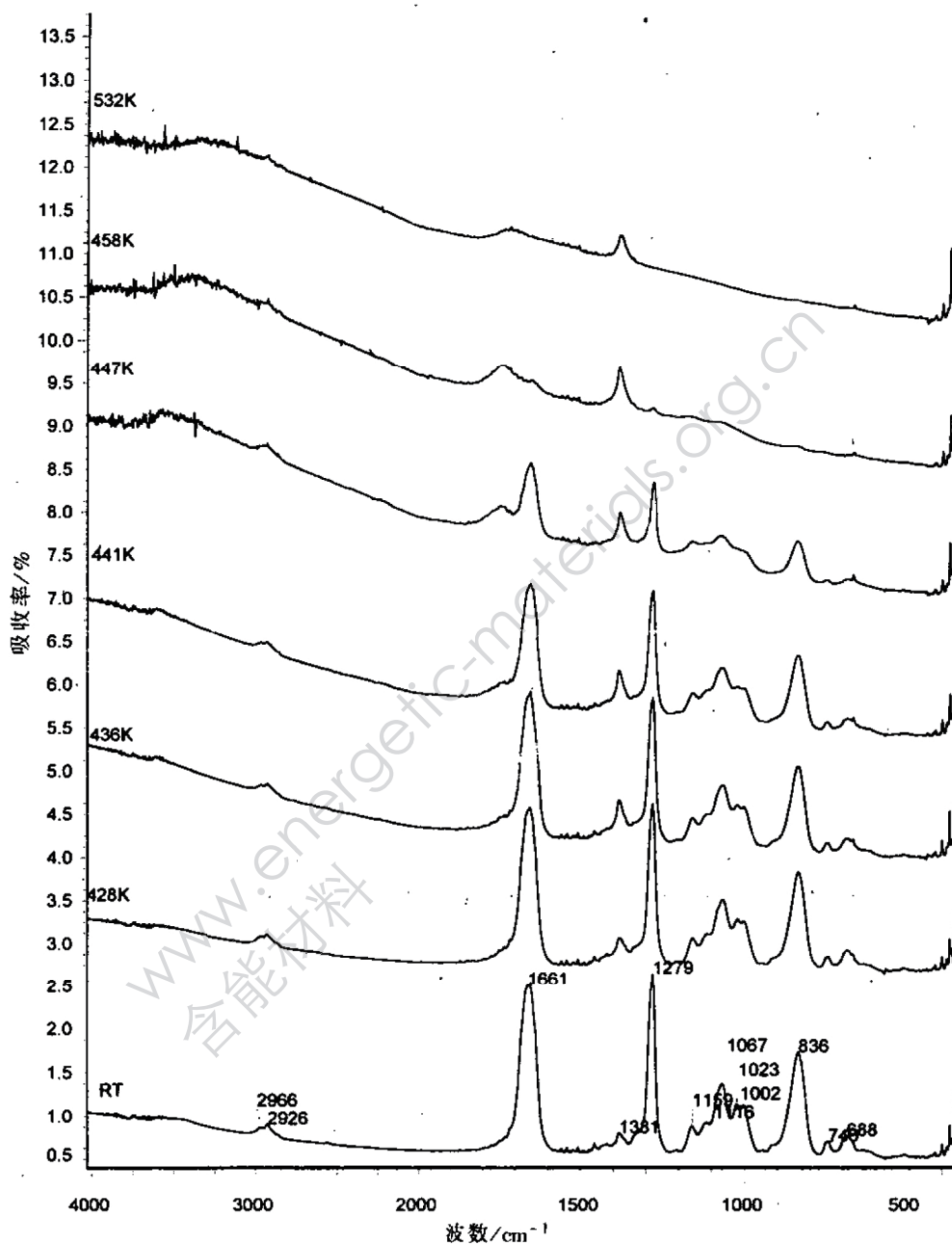


图1 NC(14.14%N)热分解凝聚相产物的典型IR谱(敞口,加热速率:  $20\text{K}\cdot\text{min}^{-1}$ )

Fig. 1 Typical IR spectra of the condensed products of  
NC (14.14%N) thermal decomposition (open, heating rate:  $20\text{K}\cdot\text{min}^{-1}$ )

表2 NC(14.14%N)IR 特征吸收峰强度随时间和温度的变化(敞口,加热速率:  $20\text{K}\cdot\text{min}^{-1}$ )Table 2 Intensity of IR characteristic absorption peaks of NC (14.14%N) vs time and temperature (open, heating rate:  $20\text{K}\cdot\text{min}^{-1}$ )

| $t/\text{min}$ | C-H<br>(3040-2813) | C=O<br>(1815-1693) | -NO <sub>2</sub><br>(1309-1253) | C-O-C<br>(1193-957) | -NO <sub>2</sub><br>(905-777) |       |       |       |       |       |       |       |       |       |
|----------------|--------------------|--------------------|---------------------------------|---------------------|-------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 0.28           | 11.83              | 0.00               | 44.15                           | 82.89               | 59.04                         |       |       |       |       |       |       |       |       |       |
| 0.84           | 11.82              | 0.69               | 44.44                           | 82.69               | 59.69                         |       |       |       |       |       |       |       |       |       |
| 1.40           | 11.80              | 1.26               | 44.61                           | 82.49               | 58.98                         |       |       |       |       |       |       |       |       |       |
| 1.95           | 11.79              | 2.05               | 44.43                           | 82.41               | 58.73                         |       |       |       |       |       |       |       |       |       |
| 2.51           | 11.77              | 2.60               | 44.44                           | 82.17               | 58.82                         |       |       |       |       |       |       |       |       |       |
| 3.07           | 11.74              | 3.38               | 44.50                           | 82.09               | 58.70                         |       |       |       |       |       |       |       |       |       |
| 3.63           | 11.84              | 4.06               | 44.08                           | 81.88               | 58.53                         |       |       |       |       |       |       |       |       |       |
| 4.19           | 11.76              | 4.71               | 43.76                           | 81.83               | 58.28                         |       |       |       |       |       |       |       |       |       |
| 4.74           | 11.75              | 5.35               | 43.70                           | 81.60               | 57.96                         |       |       |       |       |       |       |       |       |       |
| 5.30           | 11.71              | 6.12               | 43.29                           | 81.47               | 57.78                         |       |       |       |       |       |       |       |       |       |
| 5.86           | 11.63              | 6.90               | 42.85                           | 81.18               | 57.20                         |       |       |       |       |       |       |       |       |       |
| 6.42           | 11.53              | 7.96               | 41.98                           | 80.95               | 56.39                         |       |       |       |       |       |       |       |       |       |
| 6.70           | 11.42              | 8.62               | 41.74                           | 80.66               | 55.82                         |       |       |       |       |       |       |       |       |       |
| 6.98           | 11.26              | 9.67               | 41.25                           | 80.28               | 55.06                         |       |       |       |       |       |       |       |       |       |
| 7.25           | 10.93              | 11.40              | 41.01                           | 79.32               | 53.55                         |       |       |       |       |       |       |       |       |       |
| 7.53           | 10.38              | 14.08              | 37.54                           | 77.07               | 50.22                         |       |       |       |       |       |       |       |       |       |
| 7.81           | 9.96               | 18.01              | 33.62                           | 71.41               | 45.17                         |       |       |       |       |       |       |       |       |       |
| 8.09           | 9.61               | 25.09              | 25.85                           | 55.83               | 35.01                         |       |       |       |       |       |       |       |       |       |
| 8.37           | 8.97               | 38.13              | 12.90                           | 30.15               | 16.23                         |       |       |       |       |       |       |       |       |       |
| 8.65           | 9.06               | 42.19              | 4.08                            | 14.77               | 4.50                          |       |       |       |       |       |       |       |       |       |
| 8.93           | 6.47               | 41.61              | 1.13                            | 9.72                | 1.11                          |       |       |       |       |       |       |       |       |       |
| 9.21           | 6.52               | 40.85              | 0.22                            | 7.11                | 0.17                          |       |       |       |       |       |       |       |       |       |
| 9.49           | 6.66               | 40.32              | 0.07                            | 5.54                | 0.00                          |       |       |       |       |       |       |       |       |       |
| 9.76           | 6.71               | 39.59              | 0.06                            | 4.53                |                               |       |       |       |       |       |       |       |       |       |
| 10.04          | 6.10               | 38.64              | 0.05                            | 3.77                |                               |       |       |       |       |       |       |       |       |       |
| 10.32          | 6.62               | 37.76              | 0.00                            | 3.14                |                               |       |       |       |       |       |       |       |       |       |
| 10.60          | 5.11               | 37.50              | 0.03                            | 2.53                |                               |       |       |       |       |       |       |       |       |       |
| 10.88          | 4.93               | 36.98              | 0.02                            | 2.13                |                               |       |       |       |       |       |       |       |       |       |
| 11.16          | 3.15               | 36.51              | 0.05                            | 1.77                |                               |       |       |       |       |       |       |       |       |       |
| 11.38          | 5.87               | 36.01              | 0.05                            | 1.65                |                               |       |       |       |       |       |       |       |       |       |
| 11.66          | 4.47               | 35.62              | 0.07                            | 1.08                |                               |       |       |       |       |       |       |       |       |       |
| 11.94          | 5.76               | 34.86              | 0.09                            | 0.90                |                               |       |       |       |       |       |       |       |       |       |
| 12.22          | 5.63               | 34.52              | 0.08                            | 0.53                |                               |       |       |       |       |       |       |       |       |       |
| 12.50          | 5.09               | 34.15              | 0.09                            | 0.28                |                               |       |       |       |       |       |       |       |       |       |
| 12.78          | 4.53               | 33.84              | 0.09                            | 0.12                |                               |       |       |       |       |       |       |       |       |       |
| $t/\text{min}$ | 0                  | 1                  | 2                               | 3                   | 4                             | 5     | 6     | 7     | 8     | 9     | 10    | 11    | 12    | 13    |
| $T/\text{K}$   | 298.7              | 309.0              | 324.2                           | 341.5               | 359.7                         | 378.4 | 397.1 | 416.3 | 435.3 | 454.5 | 473.7 | 493.0 | 512.2 | 532.3 |

表 3 NC(13.54%N)IR 特征吸收峰强度随时间和温度的变化(敞口,加热速率:  $20\text{K}\cdot\text{min}^{-1}$ )Table 3 Intensity of IR characteristic absorption peaks of NC (13.54%N) vs time and temperature (open, heating rate :  $20\text{K}\cdot\text{min}^{-1}$ )

| $t/\text{min}$ | C-H<br>(3040-2813) | C=O<br>(1815-1693) | -NO <sub>2</sub><br>(1309-1253) | C-O-C<br>(1193-957) | -NO <sub>2</sub><br>(905-777) |       |       |       |       |       |       |       |       |       |
|----------------|--------------------|--------------------|---------------------------------|---------------------|-------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 0.22           | 6.54               | 0.00               | 22.66                           | 41.36               | 27.66                         |       |       |       |       |       |       |       |       |       |
| 0.79           | 6.57               | 0.07               | 22.61                           | 41.21               | 27.61                         |       |       |       |       |       |       |       |       |       |
| 1.35           | 6.58               | 0.45               | 22.52                           | 41.22               | 27.65                         |       |       |       |       |       |       |       |       |       |
| 1.91           | 6.55               | 0.79               | 22.50                           | 41.19               | 27.71                         |       |       |       |       |       |       |       |       |       |
| 2.47           | 6.53               | 1.10               | 22.44                           | 41.11               | 27.65                         |       |       |       |       |       |       |       |       |       |
| 3.03           | 6.55               | 1.49               | 22.35                           | 41.04               | 27.62                         |       |       |       |       |       |       |       |       |       |
| 3.59           | 6.54               | 1.86               | 22.28                           | 40.97               | 27.65                         |       |       |       |       |       |       |       |       |       |
| 4.15           | 6.58               | 2.22               | 22.16                           | 40.90               | 27.60                         |       |       |       |       |       |       |       |       |       |
| 4.71           | 6.57               | 2.61               | 22.08                           | 40.91               | 27.51                         |       |       |       |       |       |       |       |       |       |
| 5.27           | 6.57               | 3.03               | 21.91                           | 40.80               | 27.33                         |       |       |       |       |       |       |       |       |       |
| 5.83           | 6.54               | 3.56               | 21.72                           | 40.80               | 27.09                         |       |       |       |       |       |       |       |       |       |
| 6.39           | 6.45               | 4.16               | 21.38                           | 40.63               | 26.78                         |       |       |       |       |       |       |       |       |       |
| 6.67           | 6.38               | 4.56               | 21.08                           | 40.47               | 26.45                         |       |       |       |       |       |       |       |       |       |
| 6.95           | 6.32               | 5.07               | 20.66                           | 40.20               | 25.92                         |       |       |       |       |       |       |       |       |       |
| 7.23           | 6.15               | 5.97               | 20.03                           | 39.61               | 25.15                         |       |       |       |       |       |       |       |       |       |
| 7.51           | 5.90               | 7.25               | 18.86                           | 38.25               | 23.66                         |       |       |       |       |       |       |       |       |       |
| 7.79           | 5.62               | 9.32               | 16.36                           | 34.29               | 20.50                         |       |       |       |       |       |       |       |       |       |
| 8.07           | 4.94               | 12.82              | 12.25                           | 26.93               | 15.36                         |       |       |       |       |       |       |       |       |       |
| 8.35           | 4.45               | 18.05              | 6.35                            | 16.18               | 7.46                          |       |       |       |       |       |       |       |       |       |
| 8.63           | 3.81               | 19.83              | 2.04                            | 9.47                | 2.15                          |       |       |       |       |       |       |       |       |       |
| 8.91           | 3.35               | 19.65              | 0.42                            | 6.77                | 0.39                          |       |       |       |       |       |       |       |       |       |
| 9.19           | 2.96               | 19.17              | 0.10                            | 5.40                | 0.03                          |       |       |       |       |       |       |       |       |       |
| 9.47           | 3.04               | 18.74              | 0.04                            | 4.60                | 0.00                          |       |       |       |       |       |       |       |       |       |
| 9.75           | 2.82               | 18.30              | 0.04                            | 3.89                |                               |       |       |       |       |       |       |       |       |       |
| 10.03          | 2.79               | 17.91              | 0.03                            | 3.37                |                               |       |       |       |       |       |       |       |       |       |
| 10.31          | 2.55               | 17.55              | 0.03                            | 2.89                |                               |       |       |       |       |       |       |       |       |       |
| 10.59          | 2.73               | 17.18              | 0.04                            | 2.54                |                               |       |       |       |       |       |       |       |       |       |
| 10.87          | 2.91               | 16.85              | 0.04                            | 2.17                |                               |       |       |       |       |       |       |       |       |       |
| 11.15          | 2.59               | 16.49              | 0.04                            | 1.91                |                               |       |       |       |       |       |       |       |       |       |
| 11.38          | 2.81               | 16.21              | 0.04                            | 1.69                |                               |       |       |       |       |       |       |       |       |       |
| 11.66          | 2.32               | 16.10              | 0.04                            | 1.50                |                               |       |       |       |       |       |       |       |       |       |
| 11.94          | 2.11               | 15.91              | 0.04                            | 1.30                |                               |       |       |       |       |       |       |       |       |       |
| 12.22          | 2.04               | 15.71              | 0.04                            | 1.16                |                               |       |       |       |       |       |       |       |       |       |
| 12.50          | 2.29               | 15.52              | 0.04                            | 1.00                |                               |       |       |       |       |       |       |       |       |       |
| 12.78          | 2.29               | 15.36              | 0.04                            | 0.88                |                               |       |       |       |       |       |       |       |       |       |
| $t/\text{min}$ | 0                  | 1                  | 2                               | 3                   | 4                             | 5     | 6     | 7     | 8     | 9     | 10    | 11    | 12    | 13    |
| $T/\text{K}$   | 299.7              | 309.5              | 324.5                           | 341.0               | 359.2                         | 377.8 | 396.9 | 416.1 | 435.5 | 454.3 | 473.6 | 493.1 | 512.1 | 532.3 |



表4 NC(12.97%N)IR 特征吸收峰强度随时间和温度的变化(敞口,加热速率:  $20\text{K}\cdot\text{min}^{-1}$ )Table 4 Intensity of the IR characteristic absorption peaks of NC (12.97%N) vs time and temperature (open, heating rate:  $20\text{K}\cdot\text{min}^{-1}$ )

| $t/\text{min}$ | C-H<br>(3040-2813) | C=O<br>(1815-1693) | -NO <sub>2</sub><br>(1309-1253) | C-O-C<br>(1193-957) | -NO <sub>2</sub><br>(905-777) |       |       |       |       |       |       |       |       |       |
|----------------|--------------------|--------------------|---------------------------------|---------------------|-------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 0.28           | 8.04               | 0.00               | 21.79                           | 41.38               | 25.32                         |       |       |       |       |       |       |       |       |       |
| 0.84           | 8.02               | 0.24               | 21.70                           | 41.28               | 25.31                         |       |       |       |       |       |       |       |       |       |
| 1.40           | 7.99               | 0.49               | 21.69                           | 41.21               | 25.34                         |       |       |       |       |       |       |       |       |       |
| 1.95           | 7.97               | 0.83               | 21.63                           | 41.13               | 25.39                         |       |       |       |       |       |       |       |       |       |
| 2.51           | 7.96               | 1.11               | 21.58                           | 41.08               | 25.39                         |       |       |       |       |       |       |       |       |       |
| 3.07           | 7.98               | 1.41               | 21.52                           | 40.99               | 25.38                         |       |       |       |       |       |       |       |       |       |
| 3.63           | 7.99               | 1.70               | 21.42                           | 40.91               | 25.39                         |       |       |       |       |       |       |       |       |       |
| 4.19           | 7.99               | 2.02               | 21.33                           | 40.84               | 25.38                         |       |       |       |       |       |       |       |       |       |
| 4.74           | 7.94               | 2.36               | 21.18                           | 40.77               | 25.30                         |       |       |       |       |       |       |       |       |       |
| 5.30           | 7.96               | 2.73               | 21.02                           | 40.67               | 25.17                         |       |       |       |       |       |       |       |       |       |
| 5.86           | 7.90               | 3.23               | 20.81                           | 40.65               | 25.00                         |       |       |       |       |       |       |       |       |       |
| 6.42           | 7.83               | 3.79               | 20.45                           | 40.51               | 24.66                         |       |       |       |       |       |       |       |       |       |
| 6.70           | 7.73               | 4.18               | 20.16                           | 40.35               | 24.34                         |       |       |       |       |       |       |       |       |       |
| 6.98           | 7.62               | 4.72               | 19.76                           | 40.06               | 23.84                         |       |       |       |       |       |       |       |       |       |
| 7.25           | 7.52               | 5.45               | 19.14                           | 39.50               | 23.07                         |       |       |       |       |       |       |       |       |       |
| 7.53           | 7.22               | 6.57               | 18.00                           | 38.01               | 21.75                         |       |       |       |       |       |       |       |       |       |
| 7.81           | 6.96               | 8.40               | 15.61                           | 33.88               | 18.92                         |       |       |       |       |       |       |       |       |       |
| 8.09           | 6.46               | 11.92              | 11.49                           | 26.75               | 13.92                         |       |       |       |       |       |       |       |       |       |
| 8.37           | 5.86               | 16.24              | 6.18                            | 17.43               | 7.09                          |       |       |       |       |       |       |       |       |       |
| 8.65           | 5.02               | 17.75              | 2.22                            | 11.08               | 2.29                          |       |       |       |       |       |       |       |       |       |
| 8.93           | 4.58               | 17.58              | 0.53                            | 8.15                | 0.47                          |       |       |       |       |       |       |       |       |       |
| 9.21           | 4.53               | 17.16              | 0.12                            | 6.52                | 0.02                          |       |       |       |       |       |       |       |       |       |
| 9.49           | 4.19               | 16.58              | 0.07                            | 5.42                | 0.00                          |       |       |       |       |       |       |       |       |       |
| 9.76           | 4.24               | 16.13              | 0.06                            | 4.45                |                               |       |       |       |       |       |       |       |       |       |
| 10.04          | 4.21               | 15.70              | 0.06                            | 3.72                |                               |       |       |       |       |       |       |       |       |       |
| 10.32          | 4.12               | 15.25              | 0.06                            | 3.15                |                               |       |       |       |       |       |       |       |       |       |
| 10.60          | 3.83               | 14.81              | 0.07                            | 2.66                |                               |       |       |       |       |       |       |       |       |       |
| 10.88          | 3.92               | 14.48              | 0.07                            | 2.26                |                               |       |       |       |       |       |       |       |       |       |
| 11.16          | 3.80               | 14.12              | 0.06                            | 1.95                |                               |       |       |       |       |       |       |       |       |       |
| 11.38          | 3.53               | 13.92              | 0.06                            | 1.70                |                               |       |       |       |       |       |       |       |       |       |
| 11.66          | 3.77               | 13.64              | 0.06                            | 1.47                |                               |       |       |       |       |       |       |       |       |       |
| 11.94          | 3.39               | 13.36              | 0.07                            | 1.25                |                               |       |       |       |       |       |       |       |       |       |
| 12.22          | 3.51               | 13.16              | 0.05                            | 1.08                |                               |       |       |       |       |       |       |       |       |       |
| 12.50          | 3.35               | 12.98              | 0.07                            | 0.95                |                               |       |       |       |       |       |       |       |       |       |
| 12.78          | 3.34               | 12.78              | 0.06                            | 0.77                |                               |       |       |       |       |       |       |       |       |       |
| $t/\text{min}$ | 0                  | 1                  | 2                               | 3                   | 4                             | 5     | 6     | 7     | 8     | 9     | 10    | 11    | 12    | 13    |
| $T/\text{K}$   | 299.6              | 309.4              | 324.2                           | 341.2               | 359.3                         | 377.9 | 396.9 | 416.1 | 435.0 | 454.4 | 473.5 | 492.9 | 512.0 | 532.1 |

表 5 NC(11.92%N) IR 特征吸收峰强度随时间和温度的变化(敞口,加热速率:  $20\text{K}\cdot\text{min}^{-1}$ )Table 5 Intensity of the IR characteristic absorption peaks of NC (11.92%N) vs time and temperature (open, heating rate :  $20\text{K}\cdot\text{min}^{-1}$ )

| $t/\text{min}$ | C-H<br>(3040-2813) | C=O<br>(1815-1693) | -NO <sub>2</sub><br>(1309-1253) | C-O-C<br>(1193-957) | -NO <sub>2</sub><br>(905-777) |       |       |       |       |       |       |       |       |       |
|----------------|--------------------|--------------------|---------------------------------|---------------------|-------------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 0.28           | 6.42               | 0.00               | 18.50                           | 39.58               | 20.83                         |       |       |       |       |       |       |       |       |       |
| 0.84           | 6.40               | 0.15               | 18.45                           | 39.49               | 20.91                         |       |       |       |       |       |       |       |       |       |
| 1.40           | 6.42               | 0.35               | 18.39                           | 39.38               | 20.95                         |       |       |       |       |       |       |       |       |       |
| 1.95           | 6.41               | 0.53               | 18.35                           | 39.26               | 21.01                         |       |       |       |       |       |       |       |       |       |
| 2.51           | 6.40               | 0.71               | 18.28                           | 39.16               | 21.03                         |       |       |       |       |       |       |       |       |       |
| 3.07           | 6.40               | 0.91               | 18.20                           | 39.07               | 21.10                         |       |       |       |       |       |       |       |       |       |
| 3.63           | 6.43               | 1.07               | 18.14                           | 38.95               | 21.18                         |       |       |       |       |       |       |       |       |       |
| 4.19           | 6.39               | 1.27               | 18.06                           | 38.85               | 21.21                         |       |       |       |       |       |       |       |       |       |
| 4.74           | 6.38               | 1.51               | 17.97                           | 38.74               | 21.20                         |       |       |       |       |       |       |       |       |       |
| 5.30           | 6.37               | 1.82               | 17.83                           | 38.64               | 21.15                         |       |       |       |       |       |       |       |       |       |
| 5.86           | 6.38               | 2.29               | 17.60                           | 38.64               | 20.91                         |       |       |       |       |       |       |       |       |       |
| 6.42           | 6.23               | 2.99               | 17.17                           | 38.47               | 20.40                         |       |       |       |       |       |       |       |       |       |
| 6.70           | 6.20               | 3.41               | 16.84                           | 38.31               | 19.99                         |       |       |       |       |       |       |       |       |       |
| 6.98           | 6.06               | 3.93               | 16.38                           | 38.03               | 19.42                         |       |       |       |       |       |       |       |       |       |
| 7.25           | 6.01               | 4.57               | 15.64                           | 37.36               | 18.53                         |       |       |       |       |       |       |       |       |       |
| 7.53           | 5.82               | 5.45               | 14.40                           | 35.74               | 17.08                         |       |       |       |       |       |       |       |       |       |
| 7.81           | 6.00               | 7.20               | 12.34                           | 31.93               | 14.41                         |       |       |       |       |       |       |       |       |       |
| 8.09           | 5.49               | 10.15              | 9.13                            | 26.05               | 10.36                         |       |       |       |       |       |       |       |       |       |
| 8.37           | 5.46               | 12.75              | 5.28                            | 19.36               | 5.63                          |       |       |       |       |       |       |       |       |       |
| 8.65           | 4.72               | 13.75              | 2.11                            | 14.25               | 2.13                          |       |       |       |       |       |       |       |       |       |
| 8.93           | 4.69               | 13.84              | 0.45                            | 11.00               | 0.40                          |       |       |       |       |       |       |       |       |       |
| 9.21           | 3.98               | 13.55              | 0.06                            | 8.43                | 0.00                          |       |       |       |       |       |       |       |       |       |
| 9.49           | 3.89               | 12.94              | 0.03                            | 6.06                |                               |       |       |       |       |       |       |       |       |       |
| 9.76           | 3.73               | 12.38              | 0.04                            | 4.23                |                               |       |       |       |       |       |       |       |       |       |
| 10.04          | 3.31               | 11.87              | 0.05                            | 3.12                |                               |       |       |       |       |       |       |       |       |       |
| 10.32          | 3.40               | 11.43              | 0.04                            | 2.43                |                               |       |       |       |       |       |       |       |       |       |
| 10.60          | 3.44               | 11.04              | 0.05                            | 1.96                |                               |       |       |       |       |       |       |       |       |       |
| 10.88          | 3.17               | 10.65              | 0.04                            | 1.56                |                               |       |       |       |       |       |       |       |       |       |
| 11.16          | 2.69               | 10.39              | 0.04                            | 1.24                |                               |       |       |       |       |       |       |       |       |       |
| 11.38          | 2.63               | 10.16              | 0.04                            | 1.04                |                               |       |       |       |       |       |       |       |       |       |
| 11.66          | 3.00               | 9.94               | 0.06                            | 0.82                |                               |       |       |       |       |       |       |       |       |       |
| 11.94          | 3.20               | 9.76               | 0.06                            | 0.67                |                               |       |       |       |       |       |       |       |       |       |
| 12.22          | 2.95               | 9.53               | 0.04                            | 0.49                |                               |       |       |       |       |       |       |       |       |       |
| 12.50          | 2.47               | 9.37               | 0.06                            | 0.36                |                               |       |       |       |       |       |       |       |       |       |
| 12.78          | 2.94               | 9.23               | 0.05                            | 0.24                |                               |       |       |       |       |       |       |       |       |       |
| $t/\text{min}$ | 0                  | 1                  | 2                               | 3                   | 4                             | 5     | 6     | 7     | 8     | 9     | 10    | 11    | 12    | 13    |
| $T/\text{K}$   | 298.7              | 308.7              | 323.6                           | 340.6               | 358.9                         | 377.9 | 396.8 | 415.9 | 435.0 | 454.4 | 473.6 | 492.9 | 511.8 | 532.1 |



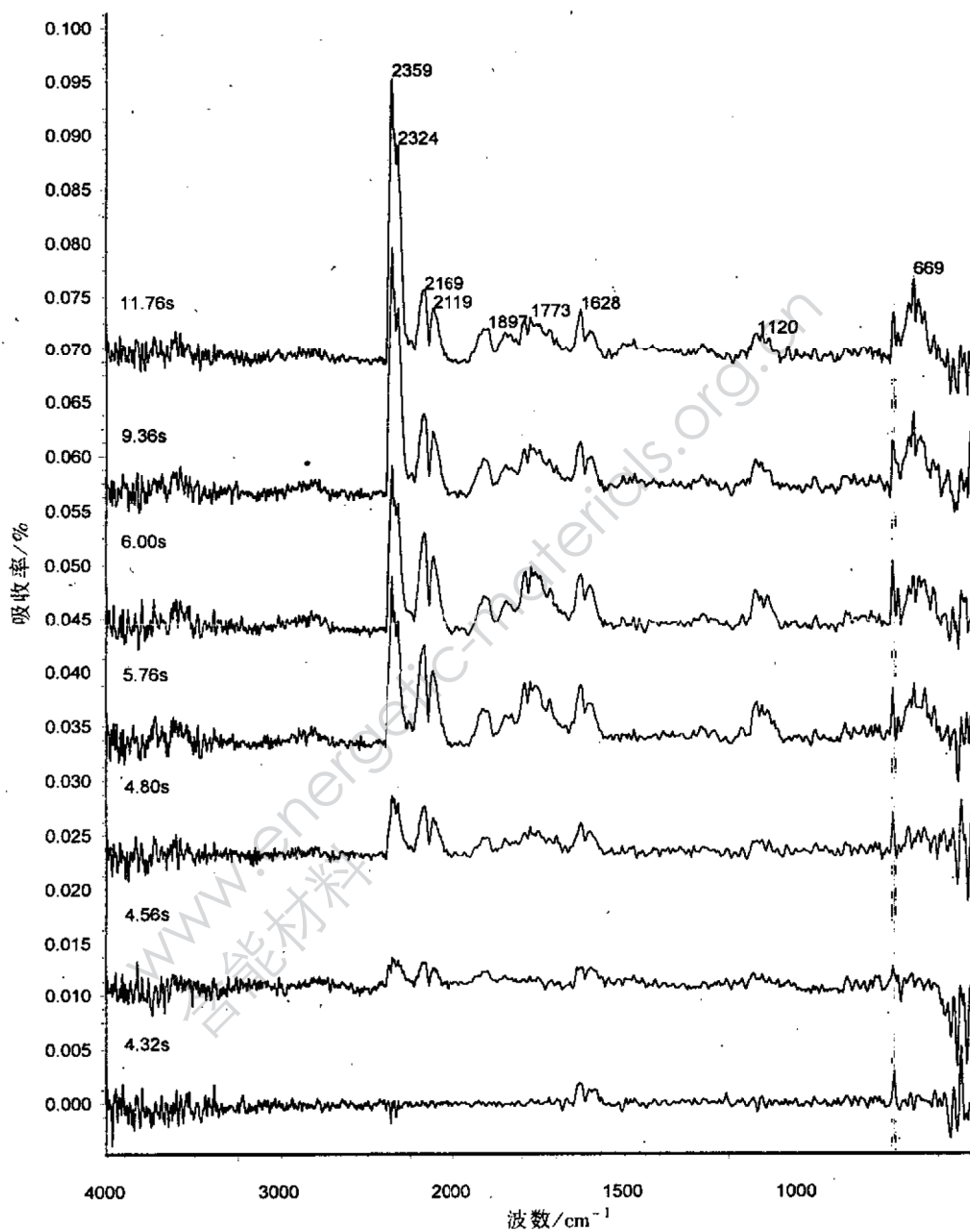


图2 NC(13.78%N)快速热裂解气相产物的 IR 谱(加热速率:  $50\text{K}\cdot\text{s}^{-1}$ )

Fig.2 IR spectra of rapid-thermolysis gaseous products of NC

(13.78%N) (heating rate:  $50\text{K}\cdot\text{s}^{-1}$ )

表 6 NC(13.78%N)快速热裂解气相产物的 IR 特征吸收峰频率和绝对强度

Table 6 Frequency and absolute intensity of IR characteristic absorption peaks of rapid-thermolysis gaseous products of NC (13.78%N)

| 气相产物          | 频率/ $\text{cm}^{-1}$ | 绝对强度/ $\text{cm}^{-2} \cdot \text{MPa}^{-1}$ |
|---------------|----------------------|----------------------------------------------|
| $\text{CO}_2$ | 2349                 | 25800                                        |
| CO            | 2143                 | 2680                                         |
| NO            | 1876                 | 1330                                         |
| HCOOH         | 1790                 | 7590                                         |
| $\text{NO}_2$ | 1621                 | 14190                                        |

表 7 NC(13.78%N)快速热裂解气相产物的组成随时间的变化(加热速率:  $50\text{K} \cdot \text{s}^{-1}$ )Table 7 Composition of rapid-thermolysis gaseous products of NC (13.78%N) vs time (heating rate:  $50\text{K} \cdot \text{s}^{-1}$ )

| $t/\text{s}$ | 气相产物组成/ $\times 10^{-4} \text{MPa}$ |       |       |       |               |
|--------------|-------------------------------------|-------|-------|-------|---------------|
|              | $\text{CO}_2$                       | CO    | NO    | HCOOH | $\text{NO}_2$ |
| 3.84         |                                     |       |       |       | 0.037         |
| 4.08         |                                     |       |       |       | 0.058         |
| 4.32         |                                     |       |       |       | 0.092         |
| 4.56         | 0.040                               | 0.382 | 0.274 | 0.006 | 0.102         |
| 4.80         | 0.079                               | 0.660 | 0.602 | 0.017 | 0.180         |
| 5.04         | 0.146                               | 1.526 | 0.835 | 0.247 | 0.190         |
| 5.28         | 0.279                               | 2.545 | 1.549 | 0.624 | 0.201         |
| 5.52         | 0.333                               | 2.784 | 1.586 | 0.610 | 0.200         |
| 5.76         | 0.376                               | 3.168 | 0.812 | 0.646 | 0.194         |
| 6.00         | 0.396                               | 3.291 | 1.962 | 0.670 | 0.192         |
| 6.96         | 0.439                               | 3.112 | 1.913 | 0.634 | 0.195         |
| 7.92         | 0.491                               | 2.847 | 1.774 | 0.581 | 0.178         |
| 8.88         | 0.548                               | 2.769 | 1.702 | 0.556 | 0.178         |
| 9.84         | 0.598                               | 2.772 | 1.683 | 0.546 | 0.175         |
| 11.04        | 0.642                               | 2.481 | 1.677 | 0.548 | 0.170         |

表 8 NC(13.78%N)快速热裂解气相产物的组成随时间的变化(加热速率:  $100\text{K} \cdot \text{s}^{-1}$ )Table 8 Composition of the rapid-thermolysis gaseous products of NC (13.78%N) vs time (heating rate:  $100\text{K} \cdot \text{s}^{-1}$ )

| $t/\text{s}$ | 气相产物组成/ $\times 10^{-4} \text{MPa}$ |       |       |       |               |
|--------------|-------------------------------------|-------|-------|-------|---------------|
|              | $\text{CO}_2$                       | CO    | NO    | HCOOH | $\text{NO}_2$ |
| 2.16         | 0.357                               | 2.485 | 1.203 | 0.125 | 0.064         |
| 2.40         | 0.407                               | 2.515 | 1.398 | 0.273 | 0.066         |
| 2.64         | 0.419                               | 3.530 | 2.105 | 0.494 | 0.117         |
| 2.88         | 0.482                               | 3.843 | 2.293 | 0.574 | 0.130         |
| 3.12         | 0.502                               | 3.996 | 2.308 | 0.600 | 0.131         |
| 3.36         | 0.575                               | 4.276 | 2.323 | 0.644 | 0.135         |
| 3.60         | 0.555                               | 4.026 | 2.406 | 0.597 | 0.135         |
| 3.84         | 0.600                               | 3.877 | 2.323 | 0.609 | 0.132         |
| 4.08         | 0.619                               | 3.608 | 2.000 | 0.581 | 0.132         |
| 5.04         | 0.709                               | 2.937 | 1.887 | 0.448 | 0.106         |
| 6.00         | 0.821                               | 2.937 | 1.892 | 0.450 | 0.125         |

表9 NC(13.78%N)快速热裂解气相产物的组成随时间的变化(加热速率:  $140\text{K}\cdot\text{s}^{-1}$ )Table 9 Composition of rapid-thermolysis gaseous products of NC (13.78%N) vs time (heating rate:  $140\text{K}\cdot\text{s}^{-1}$ )

| $t/\text{s}$ | 气相产物组成/ $\times 10^{-4}\text{MPa}$ |             |             |                |               |
|--------------|------------------------------------|-------------|-------------|----------------|---------------|
|              | $\text{CO}_2$                      | $\text{CO}$ | $\text{NO}$ | $\text{HCOOH}$ | $\text{NO}_2$ |
| 1.68         | 0.595                              | 4.750       | 3.120       | 0.428          | 0.105         |
| 1.92         | 1.117                              | 8.396       | 4.752       | 0.588          | 0.092         |
| 2.16         | 1.041                              | 8.751       | 5.218       | 0.770          | 0.179         |
| 2.40         | 1.174                              | 9.101       | 6.489       | 1.010          | 0.254         |
| 2.64         | 1.240                              | 9.000       | 6.615       | 0.980          | 0.259         |
| 2.88         | 1.259                              | 8.981       | 6.594       | 1.000          | 0.283         |
| 3.12         | 1.257                              | 8.451       | 5.932       | 0.936          | 0.283         |
| 3.36         | 1.379                              | 8.470       | 5.947       | 0.890          | 0.279         |
| 3.60         | 1.458                              | 8.455       | 6.038       | 0.959          | 0.314         |
| 3.84         | 1.578                              | 8.205       | 6.481       | 1.000          | 0.343         |
| 4.80         | 1.880                              | 7.347       | 5.820       | 1.033          | 0.328         |
| 5.76         | 2.219                              | 6.847       | 5.956       | 1.009          | 0.390         |
| 6.00         | 2.211                              | 6.716       | 5.895       | 1.007          | 0.392         |

## 5 结 论

5.1 建立了测定 NC 热分解气、固相产物的气体原位反应池/RSFT-IR 和固体原位反应池/RSFT-IR 联用装置及分析法。

5.2 根据固体原位反应池/RSFT-IR 和气体原位反应池/RSFT-IR 联用装置的测试结果,提出了 NC 热分解机理。

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## A STUDY OF THE THERMAL DECOMPOSITION MECHANISM OF NITROCELLULOSE

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**ABSTRACT** Two simultaneous devices, the rapid thermolysis reaction cell (gas reaction cell) in situ in conjunction with rapid-scan Fourier transform infrared spectroscopy (RSFT-IR), and the solid reaction cell in situ with RSFT-IR, are constructed for measuring the gas products and condensed phase products of thermal decomposition of nitrocellulose (NC) in real time. Two methods for determining the above mentioned products are presented. Under linear temperature increase condition, the thermal decomposition reaction of NC are experimentally studied, and a mechanism for this reaction is proposed based on the results.

**KEYWORDS** mechanism, NC, rapid thermolysis reaction cell/RSFT-IR, solid reaction cell/RSFT-IR, thermal decomposition.



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