Tetrahedron Letters No.17, pp. 1641-1643, 1967. Pergamon Press Ltd. Printed in Great Britain.

PHOTOLYSIS OF n-BUTYL CYANATE

M. Hara, Y. Odaira and S. Tsutsumi
Faculty of Engineering, Osaka University
Miyakojima-ku, Osaka, Japan

(Received 18 January 1967)

The photolysis of organic nitrites and hypohalites has been studied extensively and applied to many elegant syntheses[1]. However, the photolysis of organic cyanates(ROCN), a new compound reported in recent years[2], has not been studied yet. In order to examine the photolytic behavior of organic cyanates, we have carried out the vapour phase photolysis of n-butyl cyanate.

Irradiation of a gaseous n-butyl cyanate(20 mmHg.) gave various products such as n-butane, butene-1, hydrogen cyanide, cyanogen, n-butanal and n-butanol as photolytic products, n-butyl isocyanate and n-butyl isocyanurate(cyclic trimer of n-butyl isocyanate) as photo-isomerized products, and traces of polymers*. Moreover, the reactions were photosensitized by mercury and benzene. Product yields are summarized in the next Table.

---

* The photoproducts were identified and quantitatively analyzed by g.l.c. Some of the products were converted into crystalline derivatives, which were then identified by mixing melting-point determination. All irradiations were carried out in a quarz cell using a high pressure mercury arc lamp(1 kw.) at 35°C for 12 hours. In all reaction excepting IV, the charged n-butyl cyanate was completely consumed.

Table Photolyses of n-Butyl Cyanate

eaction Conditions	Products (%)							
Added Gas	$n\text{-}C_4H_{10}$	$1\text{-}C_4H_8$	HCN	$(CN)_2$	$n\text{-}C_3H_7CHO$	$n\text{-}C_4H_9OH$	$n\text{-}C_4H_9NCO$	$(n\text{-}C_4H_9NCO)_3$
(I) None	3	2	8	3	9	7	38	39
(II) Hg	trace	trace	5 [*2]	___	8	7	40	43
III) C_6H_6 [*1]	trace	trace	trace	trace	trace	trace	46	48
(IV) O_2 [*1]	2	2	4	2	6	4	20	25

[*1] 10 mmHg.

[*2] $Hg(CN)_2$ was deposited on the walls of the reaction vessel.

The results summarized in the Table lead to three probably reaction paths.

Path A

$$\begin{aligned}
n\text{-}C_4H_9OCN &\xrightarrow{h\nu} n\text{-}C_4H_9O\cdot + \cdot CN \\
n\text{-}C_4H_9OCN + \cdot CN &\longrightarrow HCN + n\text{-}C_3H_7\dot{C}HOCN \\
n\text{-}C_4H_9O\cdot + n\text{-}C_4H_9OCN &\longrightarrow n\text{-}C_4H_9OH + n\text{-}C_3H_7\dot{C}HOCN \\
n\text{-}C_3H_7\dot{C}HOCN &\longrightarrow n\text{-}C_3H_7CHO + \cdot CN \\
2C_4H_9O\cdot &\longrightarrow n\text{-}C_3H_7CHO + n\text{-}C_4H_9OH \\
2\cdot CN &\longrightarrow (CN)_2
\end{aligned}$$

Path B

$$\begin{aligned}
n\text{-}C_4H_9OCN &\xrightarrow{h\nu} n\text{-}C_4H_9\cdot + \cdot OCN \\
n\text{-}C_4H_9OCN + \cdot OCN &\longrightarrow HOCN^{*} + n\text{-}C_3H_7\dot{C}HOCN \\
2n\text{-}C_4H_9\cdot &\longrightarrow n\text{-}C_4H_{10} + 1\text{-}C_4H_8
\end{aligned}$$

Path C

$$n\text{-}C_4H_9OCN \xrightarrow{h\nu} n\text{-}C_4H_9NCO \longrightarrow (n\text{-}C_4H_9NCO)_3$$

Among these products, the formation of hydrogen cyanide and n-butanol is typical for Path A, that of n-butane and 1-butene typical for Path B, and that of n-butyl isocyanate and isocyanurate typical for Path C.

n-Butyl cyanate has an absorption maximum at 263 mμ(ε=13) in cyclohexane

---

[*] HOCN was not detected because of its easy polymerization by light.

and at 260 mμ in THF and a strong absorption band below 220 mμ. In other experiments using the light above 250 mμ, the isomerization according to Path C was the only reaction that occurred, and the cleavage reactions following Paths A and B were not encountered. Moreover, Paths A and B were not suppressed by addition of oxygen. Therefore, these facts seem to suggest that the cleavage processes can be rationalized by postulating a high energy singlet state as an excited intermediate. On the other hand, the isomerization process may proceed through a triplet state without the intervention of radicals from the facts that this process can be sensitized by added mercury and benzene and that oxygen does supress this process.

It is interesting that, in contrast to the case of organic nitrites and hypohalites, the photolysis of n-butyl cyanate predominantly results in isomerization accompanied by other minor transformations. This could be attribut to the higher bond dissociation energies of the RO-CN and R-OCN bonds[3] as compare to RO-Cl[3] and RO-NO[4] and to the high polarity of the excited n-butyl cyanate.

Further detailed kinetic studies are in progress and will be reported in the future.

References

1. M. Akhtar, Advances in Photochemistry, Vol. II, p.263.
   Interscience Publishers, New York(1964).
2. K. A. Jensen and A. Holm, Acta Chem. Scand., **18**, 826(1964).
   K. A. Jensen, M. Due and A. Holm, Acta Chem. Scand., **19**, 438(1965).
3. L. A. Errede, J. Phys. Chem., **64**, 1031(1960).
4. M. Szwarc, Chem. Rev., **47**, 75(1950).