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Free radical mechanism for photoinduced isonitrile–nitrile isomerization in solution

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Abstract

The photoinduced isomerization reaction in benzene solution from RNC to RCN was found to follow a free radical chain mechanism, where R represented $–C(CH_3)_3$, $–CH(CH_3)_2$, $–CH_3$, $–CH_2CH_3$, and $–CH_2CH_2CH_3$, respectively. The alkyl radical intermediates R. in the isomerization reaction were detected by electron spin resonance (ESR) spectroscopy in combination with spin traps PBN and ND. Initiation of the isomerization in condensed-phase can be explained by a homolytic bond breaking between R group and nitrogen atom in the photo-irradiated isonitrile derivatives at room temperature. The products analysis by GC was also supported the conclusion of free radical chain mechanism. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Isonitrile; Photoinduced isomerization; ESR; Free radical

1. Introduction

The isonitrile–nitrile isomerization [1,2] discovered in 1873 by Weith [3] is formally a 'cationatropic 1,2-shift' [4–6]. Owing to their noncatalytic nature, the isomerizations of

$$R\overset{+}{N}\equiv\overset{-}{C}:\xrightarrow{\Delta}RC\equiv N: \qquad (1)$$

methyl and a few other simple isonitrile proved to be excellent model reactions for testing kinetic theories of unimolecular gas-phase reactions [1], thermal explosions [7], and vibrational energy transfer [8]. Recently, the isonitrile as insertion species on ligand in synthetic chemistry have received particular attention [9–11]. In the process of isonitrile–nitrile isomerization, the chiral carbon in $R^{\bullet}$ group can retain the optical activity, which points the way out for the asymmetric synthesis. As a result of prominent biochemical interest in the intrinsic quality of the bond of the isonitrile compounds, many isonitriles that originate from the marine organisms are the good broad-spectrum antibiotics [12–14] and have the potential biological activity. Therefore, it is necessary to elucidate the mechanism of the isonitrule–nitrile isomerization reaction in detail.

Kinetic parameters in the isomerization reactions from methyl isonitrile(CH_3NC) to acetonitrile (CH_3CN) and from ethyl isonitrile (CH_3CH_2NC) to propionitrile (CH_3CH_2CN) have been successfully investigated by means of HeI photoelectron spectroscopy (PES) in our laboratory [15]. Similar experiments have been systematically conducted in the $CH_3CH_2CH_2NC$, $(CH_3)_2CHNC$ and $(CH_3)_3CNC$ systems. According to the results of the PES experiments and ab initio SCF MO calculations with STO-6G basis sets, we suggested that there existed a tight hypervalent three-membered cyclic transition state in the thermal isomerization reaction from RNC to RCN [16,17], belonging to typical a-shift 1,2-isomerization.

However, a new mechanism concerning the free radical chain reaction of isonitrile–nitrile isomerization have been proposed in recent years [18–20]. First, Shultz et.al. investigated infrared laser-induced isomerization reactions of methyl isonitrile and ethyl isonitrile in gas phase [18,19]. Their results revealed that a radical channel existed in conjunction with the infrared laser-induced isomerization channel in gas phase. In solution phase also there was a report of the free radical chain mechanism in the isonitrile–nitrile isomerization of *t*-alkyl isonitriles, in which the products and the kinetics of the rearrangement of isonitriles were quantitatively analyzed in the presence of free radical inhibitors [20].

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In this paper, the free radical mechanism on the visible light-induced isonitrile–nitrile isomerization of a series of alkyl isonitriles (CH_3NC, CH_3CH_2NC, $(CH_3)_2CHNC$, $CH_3CH_2CH_2NC$, $(CH_3)_3CNC$) in benzene solution has been confirmed by spin-trap ESR and GC products analysis.

2. Experiments

2.1. Synthesis of RNC

Methyl isonitrile (CH_3NC) and ethyl isonitrile (CH_3CH_2-NC) were prepared by the method of [21]. According to the report on [22], the isopropyl and propyl isonitrile were obtained from *N*-isopropylformamide and *N*-propylformamide, respectively. *Tert*-butyl isonitrile was purchased from the Acros Chemical Company Inc. Purity of the synthesized compounds were qualified by gas–liquid chromatography and NMR (better than 99.0%).

2.2. Preparation of reaction mixture

Benzene of guaranteed reagent (GR) grade served as the solvent. Spin-traps PBN and ND were synthesized and purified by the method in literature [23] and [24], respectively. Concentrations of isonitriles in all experiments were 0.05 mol/l in the reaction mixture and the concentration of PBN is 0.01 mol/l. ND was saturated with benzene. All the samples were bubbled by highly pure N_2 for 10 min to remove O_2 before irradiated at 535 nm and the isomerization was proceeded under the protection of N_2 atmosphere. A 500 W medium pressure mercury lamp coated by a water-jacket for preventing the thermal related isonitrile–nitrile isomerization was operated as the radiation source.

2.3. EPR measurements

A Bruker ESP-300 EPR spectrometer was used to measure and evaluate the EPR spectra. All experiments were carried out at room temperature. Standard settings for series of experiments were as follows: receiver gains, 2×10^5, time constant, 20.48 ms, sweep time, 83.89 s, modulation amplitude, 0.5 G and microwave power, 12.9 mW.

2.4. GC measurements

Varian VISTA 6000 gas chromatography was applied to analyze the products. A 25 m long OV-210 capillary column was equiped, and H_2 was used as the carrier gas. The column temperature was controlled to be 50°C.

Fig. 1. ESR spectrum of radical spin adducts $[PBN\text{-}CH_3]^\bullet$ at room temperature.

Table 1
The hyperfine coupling constants for free radical adducts of $[PBN\text{-}R]^\bullet$ and $[ND\text{-}R]^\bullet$

R	$[PBN\text{-}R]^\bullet$		$[ND\text{-}R]^\bullet$	
	a_H(G)	a_N(G)	a_H(G)	a_N(G)
CH_3	2.20	13.92	–	–
CH_3CH_2	2.16	13.80	–	–
$CH_3CH_2CH_2$	2.09	13.90	–	–
$(CH_3)_2CH$	2.13	13.94	6.89	13.78
$(CH_3)_3C$	2.13	13.96	–	13.68

3. Results and discussion

3.1. Spin trap

In order to elucidate the free radical chain mechanism in the process of photoinduced alkyl isonitrile–nitrile isomerization, PBN and ND were selected as spin traps to identify the existence of the free radical intermediates. If there exists a radical chain initiation in the isomerization system, the homolytic C–N bond cleavage will take place, and then the nitroxide spin adducts $[PBN\text{-}R]^\bullet$ and $[ND\text{-}R]^\bullet$ can be detected upon the addition of spin traps PBN and ND to the photolytic RNC/benzene solution. The structural information on nitroxide was confirmed by ESR instrument. As shown in Fig. 1, a 6 line ESR spectrum was obtained when using PBN as a spin trap in CH_3NC/benzene system.

Further observation indicated that as a typical ESR spectrum of spin adduct $[PBN\text{-}R]^\bullet$ the hyperfine splitting pattern on its ESR spectra was independent of the molecular structure of free radical $R^\bullet$ so the only available information was the variety of splitting constants with different $[PBN\text{-}R]^\bullet$ that were listed in Table 1. Therefore, it is difficult to infer the molecular structure of $R^\bullet$ only on the basis of ESR spectra of spin adduct $[PBN\text{-}R]^\bullet$, where R is alkyl radical.

For the sake of getting more information about the $R^\bullet$ radicals, we used another spin trap ND to determine the character of $R^\bullet$ radicals. ESR spectrum of 6 lines (Fig. 2a) could be obtained when ND was chosen in $(CH_3)_2CHNC$/benzene system, which represented the ESR signal of spin adduct $[ND\text{-}CH(CH_3)_2]^\bullet$. Its hyperfine constants are $a_H = 6.89$ G

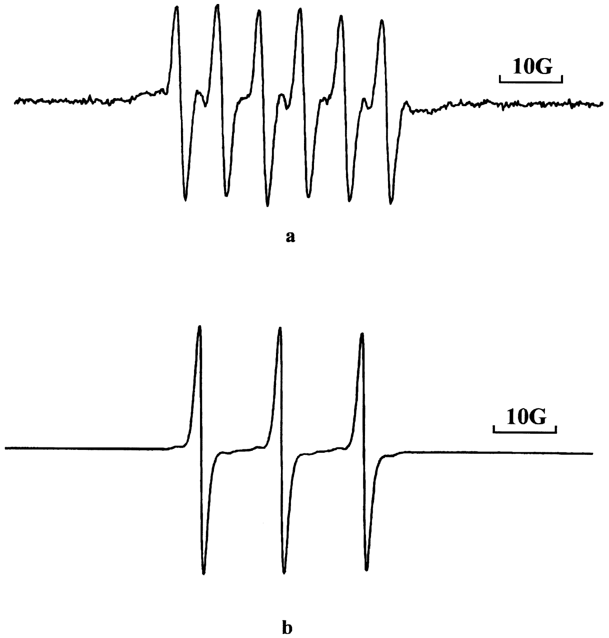

Fig. 2. ESR spectrum of radical spin adducts $[\text{ND-R}]^\bullet$ at room temperature, (a) $R = –CH(CH_3)_2$; (b) $R = –C(CH_3)_3$.

and $a_N = 13.78$ G. Another ESR signal composed of 3 lines (Fig. 2b) can be recognized as the spectrum of spin adduct $[\text{ND-C}(CH_3)]^\bullet$ with $a_N = 13.68$ G. Unfortunately, we did not get ESR spectra for spin adducts of ND with $CH_3^\bullet$, $CH_3CH_2^\bullet$ and $CH_3CH_2CH_2^\bullet$, which might be interpreted as the less stability of these three alkyl radicals comparing with that of $(CH_3)_2CH^\bullet$ and $(CH_3)_3C^\bullet$ radicals during the isonitrile–nitrile isomerization.

Above results just indicate that the C–N bond breaks and alkyl radicals are produced as a reactive intermediates in the photoinduced isonitrile–nitrile isomerization. In other words, on the basis of the results of spin trapping ESR experiments, it can be concluded that a radical channel exists in conjunction with the photoinduced isomerization channel in condensed-phase at room temperature.

3.2. Products analysis

To confirm the conclusion that there exists a free radical chain mechanism in the photoinduced isonitrile–nitrile isomerization reaction, we have designed another set of gas chromatography experiments to analyze the products of light-irradiated RNC. First, ethyl radical was introduced to CH_3NC isomerization system as a free radical initiator by means of the UV irradiation of CH_3NC/iodoethane solution. Both CH_3CN, the normal isomerization product of CH_3NC, and CH_3CH_2CN, the radical addition adduct from $CH_3CH_2^\bullet$ to CH_3NC, should be detectable, if the proposal for the free radical addition to methyl isonitrile is true in the light-irradiated CH_3NC/C_2H_5I/benzene system.

The GC experimental results, as shown in Fig. 3, convincingly supported the free radical chain mechanism as proved by our spin trapping-ESR experiments. The GC peak with a retention time of 3.54 min indicated the existence of CH_3CH_2CN in the solution of UV-irradiated mixture containing CH_3NC and C_2H_5I. Standard value for the retention time of CH_3CH_2CN, $t_R = 3.54$ min, was direct measured under the same GC experimental condition from a mixture composed of the commercial products of CH_3CH_2CN (100 μl), CH_3CH_2I (100 μl), CH_3NC (100 μl) and benzene (300 μl) (Fig. not shown).

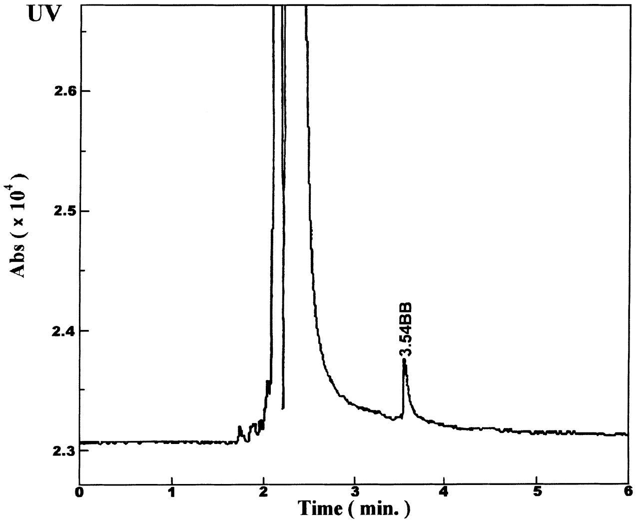

Fig. 3. Chromatogram of the product analysis by GC in the reaction of the light-irradiated benzene solution containing CH_3NC and C_2H_5I.

Furthermore, analogous results for GC products analysis of photo-induced isomerization of $CH_3CH_2CH_2NC$ and $(CH_3)_2CHNC$ were obtained in the presence of C_2H_5I, and the GC peak of the CH_3CH_2CN species was similarly identified at each reaction system (Figs. not shown). In the light of these observation together with the results drawn from spin trapping-ESR experiments, a free radical chain mechanism of photoinduced isonitrile–nitrile isomerization can be formulated as follows:

$$CH_3CH_2–I \xrightarrow{hv} CH_3CH_2^\bullet + I \quad (2)$$

$$R–NC \xrightarrow{hv} R^\bullet + NC \quad (3)$$

$$CH_3CH_2^\bullet + CN–R \rightarrow CH_3CH_2–CN + R^\bullet \quad (4)$$

$$R^\bullet + CN–R \rightarrow R–CN + R^\bullet \quad (5)$$

$R = CH_3$, $CH_3CH_2CH_2$ and $CH(CH_3)_2$.

The initial step of free radical chain reaction are presented in the formulas 2 and 3 respectively, in which the evidence on the formation of radical $R^\bullet$ is confirmed by our spin trapping experiments. Formulas 4 and 5 indicate the propagation of radical chain. The observable proof in step 4 was directly obtained from the GC experiments. It can be reasonable to consider that the reactivity of $CH_3CH_2^\bullet$ in step 4 is almost the same as that of other alkyl radicals $R^\bullet$ in step 5, where $R = CH_3$, $CH_3CH_2CH_2$ and $(CH_3)_2CH_2$ respectively, so that step 5 in reaction scheme can be rationally deduced. It should also be mentioned that the product of step 2 and 4 were detectable only upon the addition of CH_3CH_2I which was used as a probe to confirm the role of the radical $R^\bullet$ in the radical addition reactions.

4. Conclusions

The photoinduced isonitrile–nitrile isomerization reaction in benzene solution at room temperature follows the free radical mechanism. In the course of the isomerization, the C–N bond homolytically breaks and corresponding alkyl radicals are produced as the reactive intermediates.

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