Cyanation of Aromatic Olefins Induced by Plasma-Liquid Interaction

Tatsuhiko YAJIMA*, Masakazu IWASAKI and Megumu TEZUKA

Received July 13, 1994; Accepted August 24, 1994

1 INTRODUCTION

The non-equilibrium plasma generated by a glow discharge provides a unique reaction medium, and a number of intriguing organic reactions have been exploited1). These reactions are initiated by electron impact. By this way, the cyano radical (·CN) was generated from acetonitrile2-3) or cyanogen4-5) to react with coexisting olefins. However, the utility of such gas-phase reactions is limited by the need of vaporizing reactants and the complexity due to the plasmolysis of reactants themselves. Here, the plasma-liquid interaction will be introduced as a new type of synthetic measure for organic materials. In this report, the cyanation of aromatic olefins will be discussed.

2 EXPERIMENTAL

Experiments were performed with a rotary-type reaction system shown in Figure 1. A Pyrex reactor tube (45 mm diameter x 80 mm length) was connected to a vacuum system after the reactant liquid was put in. A copper coil was wound on the reactor tube. The coil was connected to a 13.56 MHz radiofrequency (rf) generator. Acetonitrile vapor was introduced into the reactor tube from the reservoir vessel. The flow rate of the vapor (rAN) was estimated from the reduced weight of the reservoir and the elapsed time (telap.). The vapor pressure was 10-10² Pa. Acetonitrile plasma was generated by the inductively coupled discharge. It contacted and reacted with the reactant liquid spreading on the inner-wall of the rotating reactor tube which was cooled by a methanol bath during the reaction. The rf power (P), rAN, telap. and the reaction temperature (t) were variable. Products were analyzed by gas chromatography (g.c.) and confirmed by g.c.-mass spectrometry.

3 RESULTS AND DISCUSSION

Various aromatic olefins in the liquid phase reacted with gaseous CH3CN plasma (Table 1).

Allylbenzene (1) gave ring-cyanized 1a and chain-cyanized 1b. 1a was a mixture of three isomers: mass spectrum, m/e (relative intensity); 1) 143 (M⁺, 100), 116 (23); 2) 143 (M⁺, 100), 116 (33); 3) 143 (M⁺, 100), 116 (19). The o : m : p ratio was almost the statistical 2 : 2 : 1. This result implies that the radical mechanism may be reasonable for this cyanation reaction. 1b may be resulted from the ·CH2CN attack onto the allyl group: mass spectrum, m/e (relative intensity) 159 (M⁺, 100), 91 (100). A typical 1a : 1b ratio was 76 : 24. However, neither products attributed to the ·CH2CN addition to the benzene ring nor products attributed to the ·CN addition to the side chain were found.

Compounds 1c and 1d; mass spectrum, m/e (relative intensity) 118 (M⁺, 70), 117 (100) were also yielded. 1d may be formed by the vapor-phase
plasmolysis of 1\(^6\)) or the photochemical di-\(\pi\)-methane rearrangement of 1 irradiated by plasma emission. However, the negligible yields of 1d may indicate the negligible contribution of these paths.

4-Phenyl-1-butene (2) also yielded two categories of main products. One contained the ring-cyanized products (2a), the mixture of isomers: mass spectrum, m/e (relative intensity): 1) 157 (M\(^+\), 37), 116 (100); 2) 157 (M\(^+\), 26), 116 (100). The other contained the chain-cyanized products (2b): mass spectrum, m/e (relative intensity) 157 (M\(^+\), 11), 91 (100). A typical 2a : 2b ratio was 68 : 32. Small amounts of intramolecular cyclization products 2c were also found: mass spectrum, m/e (relative intensity) 130 (M\(^+\), 93), 129 (100). No product attributed to \(\cdot\)CH\(_2\)CN was found.

The profile of 1-phenyl-2-butene (3) reaction was almost the same with those of reactions mentioned above. Ring-cyanized isomers (3a) and chain-cyanized isomers (3b) were the main products in the reaction mixture. The 3a : 3b ratio was typically 65 : 35. The formation of 2e was also observed though it was negligible. \(\cdot\)CH\(_2\)CN adducts were not found.

The interaction between liquid \(\alpha\)-methylstyrene and gaseous CH\(_3\)CN plasma gave only cyano-\(\alpha\)-methylstyrenes.

Through these reactions, the conversion of reactants was generally increased when P was enhanced, \(t\)\_lap was prolonged, and \(t\) rose up. No reaction occurred without plasma. Cyanation products were obtained in the reaction mixture as predominant products though the material balance should be improved (Table 1). It should be remarked that benzonitrile, the ipso-substituted product, was not detected and both starting aromatics and their cyanation products were found in the reactor tube, but not in the cold trap d. These facts strongly suggest that the cyanation mechanism in our system may be different from that of the gas-phase plasmolysis of aromatics + CH\(_3\)CN, where the ipso-substitution was very common\(^2\),\(^5\) and may contain the plasma-liquid interaction as the key step.

In conclusion, we carried out reactions of various kinds of aromatic olefins in the liquid phase contacted with gaseous CH\(_3\)CN plasma. As a result, the CN group was introduced into aromatic olefin molecules. It was suggested that \(\cdot\)CN and, in some cases, \(\cdot\)CH\(_2\)CN may play an important role for these reactions. The cyanation reactions discovered in this study are unprecedented to our knowledge. The further study is in due course.

### Table 1: Yields of cyanation products from aromatic olefins.

<table>
<thead>
<tr>
<th>Reactant, (r)_AN (^a), (P) (^b), (t)_lap (^c), (t) (^d), Conv. (^e), Products (^f)</th>
<th>Yield (^g), %</th>
<th>(\cdot)CH(_2)CN adducts, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allylbenzene</td>
<td>4.3</td>
<td>3.2</td>
</tr>
<tr>
<td>4-Phenyl-1-butene</td>
<td>3.8</td>
<td>5.4</td>
</tr>
<tr>
<td>1-Phenyl-2-butene</td>
<td>3.8</td>
<td>3.7</td>
</tr>
<tr>
<td>(\alpha)-Methylstyrene</td>
<td>4.4</td>
<td>2.7</td>
</tr>
<tr>
<td>(\cdot)CH(_2)CN</td>
<td>4.8</td>
<td>4.2</td>
</tr>
</tbody>
</table>

\(^a\)Flow rate of gaseous acetonitrile. \(^b\)Radiofrequency power. \(^c\)Elapsed time of the reaction. \(^d\)Reaction temperature. \(^e\)Conversion of the reactant. \(^f\)Regioselective ratio of cyanation products, benzen ring : side chain. \(^g\)Total yield of the cyanation products based on moles of reactant.

### REFERENCES


