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STUDY OF INTERMEDIATE SPECIES INVOLVED IN THE FORMATION OF ACRYLONITRILE—I*

ENERGIES AND ATOMIC POPULATIONS IN THE CNDO/2 APPROXIMATION

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Abstract—In the present paper we analyse several ions and radicals that can in principle react to form acrylonitrile. The analysis utilizes the total energies, dipole moments and atomic populations as given by the CNDO/2 program. It is shown that the known process $C_2H_2 + HCN \rightarrow C_3H_3N$ cannot proceed spontaneously, and the rôle played by the catalyst in propagating the reaction is related to these CNDO/2 results. The possibility of obtaining acrylonitrile via the radical reaction $CN. + C_2H_3.$ is discussed.

INTRODUCTION

SEVERAL molecular species involved in the formation of acrylonitrile have been investigated. In particular[1–4] the reaction:

$$C_2H_2 + HCN \rightarrow C_3H_3N \qquad (1)$$

and the radical reaction:

$$C_2H_3. + NC. \rightarrow C_3H_3N \qquad (2)$$

have been analyzed.

In the next section we present the total valence-electron energies, dipole moments and atomic populations of several molecules involved in these processes as reagents, products or intermediates.

All calculations were carried out with the CNDO/2 program of Pople and Segal[5] using the original parameters that these authors optimized[6] in calculations on similar molecules.

In section 3 we analyze the reactions themselves, discussing the possible role of catalysts in the light of this information and a discussion of the results is given in section 4.

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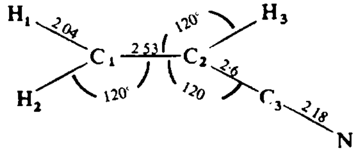
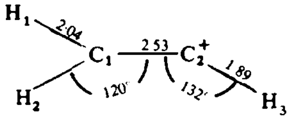
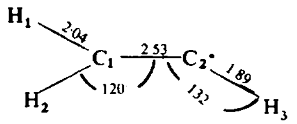
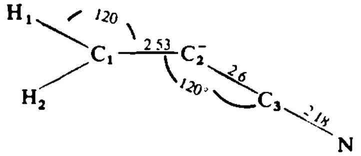
In the next paper[7] we present plots of the charge contours and spin densities and relate them to the relative stability and activity of the molecules.

CNDO/2 results

To analyze Eqn (1) we first calculated the reagents HCN and C_2H_2, the product C_3H_3N and the intermediates $C_2H_3^+$, CN^- and $C_3H_2N^-$ which could be formed in the acid attack followed by that of CN^- and *vice versa*. As the CNDO approximation is known to give inaccurate predictions for bond lengths[6] the geometrical parameters were taken from *ab-initio* calculations found in the literature.[8–10] The most relevant are reported in Table 1.

Table 1. Bond lengths in α_0 units

$\mathrm{H}\overset{2{\cdot}01}{-}\mathrm{C}\overset{2{\cdot}19}{-}\mathrm{N}$	$\mathrm{H_1}\overset{2{\cdot}00}{-}\mathrm{C_1}\overset{2{\cdot}27}{-}\mathrm{C_2}\overset{2{\cdot}00}{-}\mathrm{H_2}$
	$\mathrm{N}\overset{2{\cdot}19}{-}\mathrm{C}^-$
	$\mathrm{N}\overset{2{\cdot}19}{-}\mathrm{C}\cdot$
	

Bond lengths and bond angles utilized in the CNDO/2 calculations

The resulting energies, dipole moments and atomic populations are given in Table 2, and in Table 3 we give the corresponding heats of formation for the different processes. Thus, if the following intermediates are proposed for process (1):

$$H^+ + NC^- + C_2H_2 \rightarrow CH_2{=}C^+H + NC^- \tag{3a}$$

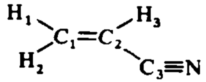
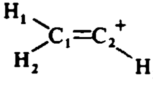
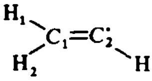
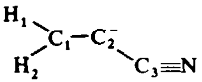
or

$$H^+ + NC^- + C_2H_2 \rightarrow H^+ + C^-H{=}CH{-}CN \tag{3b}$$

we obtain from Table 3 the following heats of formation: 0·6787 a.u. for (3a) and 0·6116 for (3b). Both processes are highly endothermic, so much so that we may say that (1) is not feasible. This is in accord with chemical intuition, because a very weak acid can hardly render (1) a spontaneous process.

Suppose that the species appearing as products in Eqns (3) are formed; for example,

TABLE 2. TOTAL ENERGY, DIPOLE MOMENT AND ATOMIC POPULATIONS CALCULATED BY THE CNDO/2 PROGRAM

Chemical species	Total energy[a]	Dipole moment[b]		Atomic populations						
		X[c]	Y	H_1	H_2	H_3	C_1	C_2	C_3	N
$H-C\equiv N$	−19·1539	2·41	0·0	0·929		—	3·980		—	5·090
$H_1-C_1\equiv C_2-H_2$	−15·3419	0·0	0·0	0·936	0·936	—	4·063	4·063	—	—
	−34·8401	−1·52	−2·48	0·974	0·984	0·972	4·011	3·994	3·916	5·145
$N\equiv C^-$	−18·1719	−3·90	0·00	—	—	—	4·579	—	—	5·420
	−15·6452	3·27	−0·15	0·789	0·749	0·821	3·999	3·640	—	—
$N\equiv C\cdot$	−18·1170	0·96	−0·01	—	—	—	3·931		—	5·068
	−16·0528	−0·58	−0·72	0·963	0·955	0·956	4·056	4·067		—
	−33·8842	−4·16	−2·67	1·100	1·098	—	4·412	4·106	3·888	5·392

[a] In atomic units

[b] In Debyes

[c] Taken as the principal axis of the molecule

CNDO/2 results for the total valence electron energy, x- and y-components of the dipole moment and total atom electron densities

TABLE 3. ENERGIES OF FORMATION (ΔE)

Reaction	ΔE (in atomic units)
$HC{\equiv}CH + HCN \rightarrow H_2C{=}CH{-}CN$	−0·3443
$HC{\equiv}CH + HCN \rightarrow CH_2{=}CH^+ + CN^-$	+0·6787
$HC{\equiv}CH + HCN \rightarrow CH^-{=}CH{-}CN + H^+$	+0·6116
$CH_2{=}CH^+ + CN^- \rightarrow CH_2{=}CH{-}CN$	−1·0230
$CH^-{=}CH{-}CN + H^+ \rightarrow CH_2{=}CH{-}CN$	−0·9559
$CH_2{=}CH. + CN. \rightarrow CH_2{=}CH{-}CN$	−0·6703

Energies of formation for the different reactions obtained from the total energies given in Table 2 for all reagents and products

by catalytic action (see discussion in next section), the following ionic reactions must be analyzed:

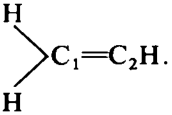
$$NC^- + C^+H{=}CH_2 \rightarrow CH_2CH{-}CN \tag{4a}$$

$$H^+ + C^-H{=}CH{-}CN \rightarrow CH_2{=}CH{-}CN \tag{4b}$$

The atomic populations in Table 2 favour both reactions, as in (4a) we have the attack of the electron-rich part of the NC^- ion which is the C atom on the most depopulated carbon of $CH_2{-}C^+H$. And from Table 2 we also gather that the ideal spot for protonation in $(C_3H_2N)^-$ is the extreme carbon with most of the excess electronic charge.

From Table 3 we get the heats of formation for processes (4a) and (4b) which are seen to be highly exothermic. As we can expect the activation barrier to be almost nil for a cation-anion reaction (see for instance the large dipole moments of the reactants in (4a) in Table 2) then if reaction (1) takes place it is a matter of propagating reactions (3a) or (3b) so that it can proceed spontaneously.

The corresponding results for the radicals that appear as reagents in Eqn (2) are also in Table 2. Here, of course, one would have to consider some way to produce the free radicals, for example, a photochemical process. But we shall only consider (2) as a single step process between the two radicals isolated in vacuum to avoid considering the multiple products that appear in most radical reactions (like dimers of $CN\cdot$, $C_2H_3\cdot$, etc).

From Table 2 we see that the dipole moments and atomic populations are such that (2) is favoured. Thus the coupling of the unpaired electrons comes from the fact that the electron-rich carbon C_2 in  $H_2C_1{=}C_2H.$ is attacked by the C extreme in $CN.$ which is slightly positive because of the nitrogen electronegativity as shown in Table 2. The reaction (2) is also exothermic.

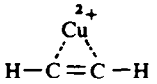
Our main interest in reaction (2) is the analysis of the spin polarization on the radicals which will be discussed in following papers, first in the CNDO/2 approximation in paper II of this series, while a future *ab-initio* study of the whole reaction path is being planned.

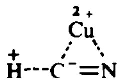
In the next section we return to reaction (1), now relating our results to the known catalytic mechanism.[2,3]

Relation to the reaction mechanism

The process described in Eqn (1) is experimentally achieved in the presence of catalysts which consist mostly of copper chlorides and copper dust in hydrous media and with some strong acid like HCl or H_3PO_4.[2–4] The acetylene and HCN molecules are adsorbed and the formation of Cu complexes for both reactants has been identified.[2,3]

Suppose that the following complexes are formed:





Then the high barrier for process (3a) is reduced. The acetylene complex implies that the C atoms are more positive than in free C_2H_2, while the proton in the other complex is rejected by the excess positive charge, thus propagating the attack of ^-CN on C_2H_2, and then from the discussion of section 2 it is an easy matter for H^+ to attack as in (4b).

On the other hand the possibility of a proton attack on free C_2H_2 cannot be excluded, especially in the presence of strong acids; thus mechanism (4a) would proceed as the attack of $^+C_2H_3$ on the electron-rich part of the complex,

$$[\mathrm{Cu—C{\equiv}N}]^+$$

thus forming acrylonitrile followed by its desorption.

In both cases our results predict that the process is not spontaneous, thus needing catalytic action in the formation of the ionic intermediates, but after they are formed the reaction path to acrylonitrile seems favourable. To confirm this we plan future *ab-initio* calculations for the whole activated complex.

CONCLUSIONS

We have analyzed reaction $HCN + C_2H_2 \rightarrow C_3H_3N$ as a two step process that is highly endothermic in the formation of the different possible ionic intermediates. Thus the use of catalysers as proposed in the literature is mostly to propagate such ions, as thereon the process is spontaneous, and the dipole moments and energies of formation are all favourable.

The radical reaction $CH. + C_2H_3.$ seems possible, and in spite of the diversity of products usually present in such cases, formation of acrylonitrile is favoured by the dipole moments and relative energies as calculated here.

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