Three Isomeric Chlorobutenynes

RAGNAR VESTIN, ASTRID BORG and TORBJÖRN LINDBLOM

Institute of Inorganic and Physical Chemistry (Catalytical Laboratory), Stockholm University, Stockholm, Sweden

We have for a long time been involved in studies on kinetics and mechanism of the aliphatic acetylene dimerization [1] in a liquid Cu(I) catalyst (used in a continuous process) according to

$$2\ HC{\equiv}CH \rightarrow CH_2{=}CH{-}C{\equiv}CH$$

Some years ago we tested a redox hypothesis for the reaction mechanism by introducing a small flow of O_2 in the entering gas. We expected to find an amount of diacetylene equivalent to the O_2 absorption and a simultaneous reduction of the monovinyl acetylene production. A completely analogous preparation of substituted diacetylenes from monoacetylenes had already been described.[2] We found out that the absorbed O_2 reacted rapidly without any appreciable formation of Cu(II) and that the formation of monovinylacetylene decreased. But to our surprise no diacetylene was found but instead a chlorohydrocarbon, formed in a reaction according to

$$2\ C_2H_2 + O_2 + HCl \rightarrow C_4H_3Cl + H_2O$$

Finlay (du Pont) [3] has made the same observations and described them carefully. The product is a chlorobutenyne, but until the present we have been dubious about the structure although Finlay suggested 2-chlorobuten-3-yne.

In an attempt to find other routes to chlorobutenyne we also studied the dehydrochlorination of 1,4-dichloro-2-butyne by alkali. Diacetylene was formed as end product but the reaction was readily shown to be consecutive. In non aqueous solution a considerable amount of alkali chloride precipitates before a noticeable amount of diacetylene is formed. Canadian [4] and Russian [5] scientists have isolated a chlorobutenyne as an intermediate in this case and both groups have considered the structure 2-chlorobuten-3-yne as proved. We also isolated a chlorobutenyne from the reaction mixture but the IR spectrum proved that the substance was *not identical* with the chlorobutenyne obtained from acetylene, HCl and oxygen with Cu(I) catalyst. At least one of the above mentioned identifications must consequently be wrong.

We therefore decided to determine how the different chlorobutenynes are distributed on the three possible structures: *cis*-1-chlorobuten-3-yne, *trans*-1-chlorobuten-3-yne, and 2-chlorobuten-3-yne.

The new results are summarized here and a more detailed report will be given later. On dehydrochlorination of 1,4-dichloro-2-butyne with alkali in homogeneous ethanol solution it is normally possible to isolate, if the reaction is interrupted before the starting material is consumed, three intermediates, chlorobutatriene,[6] *cis*- and *trans*-1-chlorobuten-3-yne besides the end product diacetylene. The yields depend in a rather complicated way on temperature, solvent, concentrations and conversion degree and we have not yet obtained a distinct picture. A low temperature, 0—10°C, promotes the formation of chlorobutatriene.

The stability of these substances is good in the gaseous and the solid state but

Table 1. Relative delays in di-ethyl-hexyl-sebacate column of chlorobutenynes, chlorobutatriene, and some other substances.

Substance	100°	50°	Substance	50°
Diacetylene	0.71	0.24	Acetylene	0.071
Ethanol	1.00	0.30	Monovinylacetylene	1.00
trans-1-Chlorobuten-3-yne	2.76	0.79	2-Chlorobuten-3-yne	7.15
Carbon tetrachloride	—	1.00	Divinylacetylene	10.93
cis-1-Chlorobuten-3-yne	3.97	1.29		
Chlorobutatriene	6.57	2.21		
1,4-Dichloro-2-butyne	55.6	—		

inferior in solution. In spite of this they can be purified by gas-liquid chromatography at a temperature up to 150°C and a retention time of 10–15 min.

Table 2. Mass spectra of three isomeric chlorobutenynes.

m/e	Relative intensities		
	2-Chloro-buten-3-yne	*trans*-1-Chloro-buten-3-yne	*cis*-1-Chloro-buten-3-yne
49	21.5	2.7	1.6
50	52.5	28.4	25.6
51	94.5	100.0	100.0
52	4	5.5	4.5
60	3	2.8	3.6
62	<1	1.4	1.2
84	1.5	0.8	0.8
85	1.5	2.1	1.9
86	100.0	100.0	95.0
87	5	5.9	6.1
88	33.5	34.3	34.2
89	1	0.7	1.3

Table 1 gives a comparison of the retentions of these substances and of some other compounds present in the reaction mixture or in the effluent gas from the continuous preparation of chlorobutenyne with Cu(I) catalyst. The figures indicate the relative delays (relation between retentions measured from the air peak) with an arbitrary standard and they are thus independent of column length, gas flow and pressure fall.

The mass spectra of the three substances (see Table 2) show the molecular ions $C_4H_3{}^{35}Cl$ and $C_4H_3{}^{37}Cl$ with the mass numbers 86 and 88 and the intensity relation 3:1. The mass spectra of these three isomers and of chlorobutatriene [6] are all rather similar, showing $C_4H_3{}^+$ as the largest fragment. (The molecular ions of chlorobutatriene seem, however, to be somewhat less stable than the others.)

IR spectra of the three gaseous substances are given in Fig. 1. The stability is acceptable for these measurements (at 25°C) but in the spectrum B the wide band at 2800–3000 cm^{-1} probably belongs to a decomposition product. All the chlorobutenynes, as distinct from chlorobutatriene, show the characteristic ≡C–H stretching vibration band of monoacetylenes at 3300 cm^{-1} which is important evidence for the structures proposed. Otherwise we consider these IR spectra only as an aid for analytical identification.

The high resolution NMR spectrum (see Fig. 2) of the chlorobutenyne originating from acetylene is of ABX type. The X part (Curve I) is an 1:2:1 triplet, a fact that can be explained by one of the three following conditions: $\nu_A = \nu_B$, $J_{AX} = J_{BX}$, $J_{AX} + J_{BX} = 0$. The AB part (curve II) — a symmetrical octet — is consistent with all these possibilities. By spin decoupling irradiation of the X part the octet is changed into a quartet (curve III) which clearly shows that $\nu_A \neq \nu_B$. The first possibility is consequently eliminated. The third possibility is excluded due to inferior agreement between measured and calculated

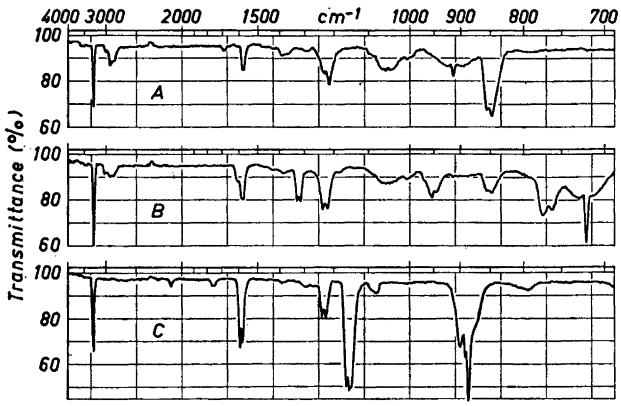

Fig. 1. IR spectra of three isomeric chlorobutenynes. Vapour mixed with He, NaCl optics, 25°C. A, B: *cis*- and *trans*-1-chlorobuten-3-yne, C: 2-chlorobuten-3-yne.

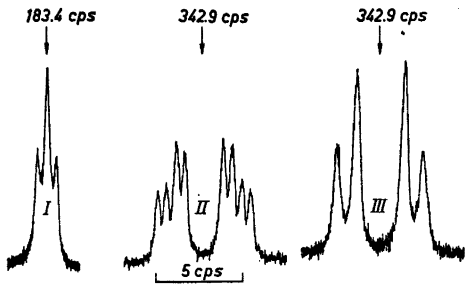

Fig. 2. High resolution NMR spectrum (Varian A60A) of 2-chlorobuten-3-yne. *Ca.* 0.3 M solution in CCl_4. I: X part. II: Original AB part. III: The AB part after spin decoupling (field sweep mode) with a difference of −159.2 cps.

intensities and the remaining solution is:

$\nu_X = 183.4$ cps, ($\delta = 3.06$ ppm), $\nu_{AB} = 342.9$ cps, ($\delta = 2.28$ ppm), $|J_{AB}| = 1.1$, $J_{AX} = J_{BX} = \pm 0.5$, $\nu_A - \nu_B = 3.6$ cps.

The low spin coupling constant J_{AB} no doubt indicates geminal hydrogen atoms as does the low value of the long range coupling constants. In monovinylacetylene a geminal coupling constant of 2.0 cps and long range coupling constants of 0.7 and 0.8 cps have been found [7] but the coupling constants of hydrogen atoms in the *cis* and *trans* positions are as high as 11.5 and 17.5 cps. The chlorobutenyne derived from acetylene is thus identified as 2-chlorobuten-3-yne.

The two chlorobutenynes from 1,4-dichloro-2-butyne, however, have a different structure. Only the *cis* and *trans* forms can be considered. There is reason to believe that the more volatile substance, corresponding to the IR curve A, is *trans*-1-chlorobuten-3-yne.

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Model Systems for Copper-Protein Interaction: Polynuclear Copper(II) Complexes of Glycylhistidylglycine

RAGNAR ÖSTERBERG and BO SJÖBERG

Department of Medical Biochemistry, University of Göteborg, Göteborg, Sweden

In an effort to gain a detailed understanding of the interactions in solution between Cu^{2+} ions and histidyl residues present in proteins [1,2] a quantitative study using a low-molecular-weight model compound, glycylhistidylglycine (H_3A^{2+}), has been performed at 25.0° in 3.0 M $NaClO_4$ medium.

Glycylhistidylglycine was obtained commercially from Yeda (Israel) and was tested for purity by paper chromatography, paper electrophoresis, and quantitative amino acid analysis. Acid-base data were recorded for values of the total concentrations of peptide (A), equal to 2.5, 10, and 20 mM, by using a glass electrode, calibrated against a hydrogen electrode. This gave the pK values 3.57, 7.54, and 8.62. When solutions of $A \sim B$ (total concentration of Cu^{2+}), were titrated with OH^- in the pH range 3 to 7, it was found — in agreement with the results of Bryce, Roeske and Gurd [3] — that the Cu(II)-induced proton dissociation of the peptide bond occurred at relatively low pH (~pH 5). Below pH 7 there was only one proton released in this manner per each peptide molecule.

Emf titrations using a copper amalgam electrode were carried out in order to give