Chemical Reaction of Metallic Copper with Imidazole†

Gi Xue,* Shangen Jiang, Xueying Huang, and Gaoguan Shi
Department of Chemistry, Nanjing University, Nanjing, The People's Republic of China
Biao Sun
Nanjing Institute of Education, Nanjing, The People's Republic of China

The chemical reaction of imidazole with metallic copper was investigated by i.r. and *X*-ray photoelectron spectroscopies. When a chemically cleaned copper disc was immersed in imidazole solution at room temperature, di-imidazolatocopper(II) formed on the surface of the copper. A reaction scheme is proposed.

Imidazole is of interest as a corrosion inhibitor for copper and alloys.[1-3] The molecular structure and anti-corrosion mechanism of imidazole have been studied by many authors, but are still not well understood.[4-7] The consensus is that imidazole is chemically adsorbed on the surface of copper oxide to form a copper–azole co-ordination film.[8-10] Imidazole is also of considerable interest as a ligand in that its presence in many biological systems provides a potential binding site for metal ions, such as Cu^{I}, Cu^{II}, Co^{II}, and Ni^{II}.[11,12] Relatively few reports exist concerning the reaction of metallic copper and imidazole. We have investigated the chemical reaction of imidazole on a chemically cleaned copper surface. It was found that a di-imidazolatocopper(II) complex formed upon immersing a metallic copper disc in an imidazole solution exposed to the air at room temperature.

Results and Discussion

The principal i.r. absorption bands of imidazole, the product of reaction of metallic copper with imidazole, and the complex prepared from copper ion and imidazole are listed in the Table.

Imidazole has strong intermolecular hydrogen bonding in the solid state.[13] The spectrum of the products of reaction of metallic copper with imidazole is very different from those of imidazole (Him) and the complex $Cu(Him)_4Cl_2$. The complete absence of both the N–H stretching frequency at 3 200 cm^{-1} and the N–H bending frequency in the region 1 450—1 400 cm^{-1} indicates the absence of the imino hydrogen in the reaction products. The analytical results for the reaction products confirm this. *X*-Ray photoelectron spectroscopy indicated that the products contain Cu^{II}. We conclude that di-imidazolatocopper(II) is formed in the reaction of metallic copper with imidazole.

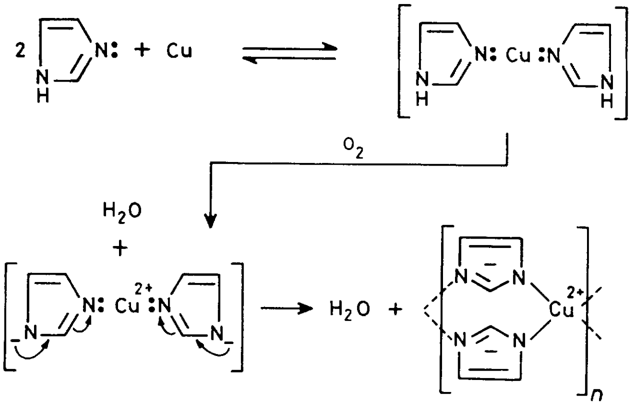
Chloroform, alcohols, acetone, or ethers could be used as media for the reaction. Water was detected as the reaction proceeded. The reaction ceased as the medium was warmed to 60 °C, or the oxygen was removed from the medium by bubbling with prepurified nitrogen.

Usually di-imidazolatocopper(II) is prepared by boiling a sufficiently basic solution of imidazole and copper ion. In our experiment the complex was formed by the reaction of metallic copper(0) and imidazole in near neutral solution at room temperature. It seems that the reaction follows the mechanism shown in the Scheme. The first step is probably attachment of the so-called 'pyridine' nitrogen of the imidazole to copper through the lone pair of electrons, forming an unstable intermediate complex. Both copper and the imine thus become more reactive. When the solution is exposed to the air, oxidation takes place, resulting in the formation of water and di-imidazolatocopper(II).

Table. Principal i.r. absorption bands (4 000—600 cm^{-1})*

Imidazole	Copper imidazolate (reaction product)	$Cu(Him)_4Cl_2$
		3 299s
3 200—	3 120w	3 119vs,br
2 400vs, br		
1 576w	1 590w	1 590w
1 540w		1 536s
	1 490s	1 493s
	1 470s	
1 448m		1 429m
1 325m	1 317m	1 335s
1 263m		1 262m
	1 242m	
1 146m	1 169m	1 141m
	1 069vs	1 068vs
1 055vs		
	949m	942m
936vs		
841m	828m	873—
756s	747s	729s,br
659s	667s	663vs
620w		609s

* S = Strong, m = medium, w = weak, br = broad, and v = very.



Scheme.

It does not seem possible that the cleaned metallic copper was first oxidized by air to copper oxides, and then reacted with imidazole, because copper oxides would form a copper–imidazole complex containing an imino group instead of di-imidazolatocopper(II) in the near-neutral medium at room temperature.[14]

---

† *Non-S.I. unit employed:* eV ≈ 1.60 × 10^{-19} J.

Di-imidazolatocopper(II) is insoluble in common solvents and generally is considered to be polymeric in nature. When a copper disc was immersed in imidazole solution without vigorous agitation, a di-imidazolatocopper(II) polymeric film formed on the surface of copper as a corrosion-inhibiting layer.

Experimental

Preparation.—The copper disc was made from 99.99% pure copper obtained from Alfa Chemicals. It was mechanically polished and chemically etched in 10% HNO_3 to remove copper oxides, repeatedly washed with distilled water, and dried in vacuum. The cleaned disc was immersed in an imidazole solution in ethanol (5% by weight) with vigorous agitation at room temperature for 3 d. It was then exposed to the air. After separation, the copper disc was found to have decreased in mass by 1.121 g, and 3.421 g of reaction product were collected. The molar ratio of the reacted copper to the reacted imidazole was 1:1.97. The reaction product is purple, and does not dissolve in common solvents (Found: C, 36.0; H, 3.05; Cu, 33.0; N, 27.6. $C_6H_6CuN_4$ requires C, 36.3; H, 3.00; Cu, 32.4; N, 28.2%).

Physical Measurements.—I.r. spectra were obtained with a Nicolet 170 SX spectrophotometer. The principal i.r. frequencies are shown in the Table. *X*-Ray photoelectron spectroscopy indicated the binding energy of Cu(2*p*) to be 935.1 eV, suggestive of Cu^{II}.

Acknowledgements

We are grateful for the support of the National Natural Science Foundation of China.

References

1 A. Farkas and P. F. Strohm, *J. Appl. Polym. Sci.*, 1968, **12**, 159.
2 G. N. Ekilik, V. P. Grigorev, and V. V. Ekilik, *Zashch. Met.*, 1978, **14**, 357.
3 C. Glandt and J. K. Gillham, *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.*, 1975, **16**, 694.
4 K. H. Wall and I. Davies, *J. Appl. Chem.*, 1965, **15**, 389.
5 H. G. Tompkins and S. P. Sharma, *Surf. Interface Anal.*, 1982, **4**, 261.
6 S. Yoshida and H. Ishida, *J. Adhesion*, 1984, **16**, 217.
7 S. Yoshida and H. Ishida, *Appl. Surface Sci.*, 1985, **20**, 497.
8 S. Yoshida and H. Ishida, *J. Mater. Sci.*, 1984, **19**, 2323.
9 S. Yoshida and H. Ishida, *J. Chem. Phys.*, 1983, **78**, 6960.
10 C. McCrory-Joy and J. M. Rosamilia, *J. Electroanal. Chem.*, 1982, **136**, 108.
11 W. J. Eilbeck, F. Holmes, and A. E. Underhill, *J. Chem. Soc. A*, 1967, 757.
12 F. Holmes, K. M. Jones, and E. G. Torrible, *J. Chem. Soc.*, 1961, 4790.
13 N. B. Colthup, L. H. Daly, and S. E. Wiberley, 'Introduction to Infrared and Raman Spectroscopy,' Academic Press, New York, 1975, p. 430.
14 M. L. Foresti, F. Pergola, and R. Guideli, *J. Electroanal. Chem. Interfacial Electrochem.*, 1980, **107**, 307.

Received 21*st July* 1987; *Paper* 7/1321