Surface Co-ordination Reactions of β-Dicarbonyl Compounds with Metallic Copper

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Surface co-ordinations of dibenzoylmethane, acetylacetone and ethyl acetoacetate with metallic copper in the presence of air have been studied by the use of surface-enhanced Raman scattering, X-ray photoelectron and infrared spectroscopies. Oxygen coadsorbed on the copper surface promoted the reactions through cleavage of the methylene C–H bond. It was found that metallic copper could promote these surface reactions with dicarbonyl compounds, while copper in higher oxidation states appeared to be inactive under the same conditions.

In previous papers[1–4] we reported that imidazole, benzimidazole and benzotriazole react with zerovalent metals, yielding azolate salts in the form of polymeric materials on the metal surfaces. Recently, we have discovered that many types of organic compounds containing polar functional groups readily react with metallic copper and silver in the presence of air. On the basis of these studies, we postulate that oxygen coadsorbed on a metal surface is a strong Brönsted or Lewis base which promotes the corresponding reaction through an oxidation step. It is remarkable that Madix and Bartean[5] once proposed a acid–base model for illustrating the reactions of esters, aldehydes and nitriles on single-crystal surfaces of metals. According to this model, the coadsorbed oxygen can show strong basicity only on certain index surfaces. Our studies, which reveal that oxygen chemisorbed either on a powdered copper surface or on a copper sheet surface has nearly the same strong basicity, led us to set up a new concept to deal with these reactions. Through extensive studies focused on many kinds of polar organic compounds, we assume that both the chemisorbed reactants and the metal atoms on the surface layers are activated through co-ordination bonding and that electron transfer may cause the fission of some certain bonds.

β-Carbonyl compounds such as dibenzoylmethane, acetylacetone (Hacac) and ethyl acetoacetate are commonly used in organic chemistry and are well known as ligands.[6] However, little attention has been paid to their direct reactions with transition metals in the zero oxidation state. A report on the co-ordination of copper(0) with α-dicarbonyl compounds[7] urged us to investigate this field in more detail.

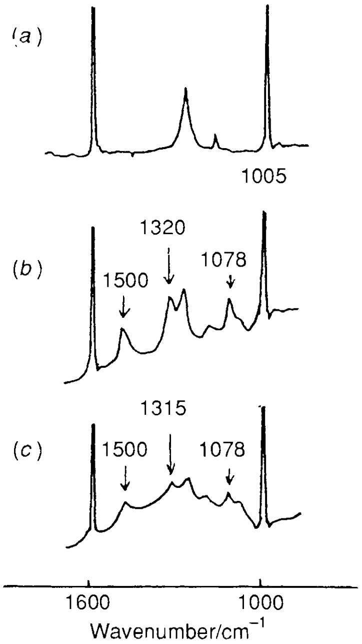


Fig. 1 Raman spectra of the reaction of dibenzoylmethane on a metallic copper surface: (*a*) normal spectrum of neat dibenzoylmethane; (*b*) SERS spectrum of chemisorbed material on copper foil from dibenzoylmethane solution; and (*c*) normal spectrum of commercial copper–dibenzoylmethane salt

Results and Discussion

Fig. 1 compares the surface-enhanced Raman scattering (SERS) spectrum of dibenzoylmethane chemisorbed on copper and the normal Raman spectra of dibenzoylmethane and of its copper salt in region 1000–1700 cm^{-1}. These spectra show bands near 1000 and 1600 cm^{-1}, which were assigned to the ring-breathing and -stretching vibration modes respectively. The appearance of new bands near 1078, 1320 and 1500 cm^{-1} in the SERS spectrum indicates that dibenzoylmethane chemically reacted with the copper surface to form a salt. These bands do appear in the normal Raman spectrum of the model copper salt, as shown in Fig. 1(*c*).

In order to provide a more complete picture of the surface reaction, copper powder was mixed with dibenzoylmethane solution. After separation, a green powder was obtained. Its IR spectrum [Fig. 2(*b*)] was compared with that of neat dibenzoylmethane and of the commercial copper–dibenzoylmethane salt [Fig. 2(*a*) and (*c*) respectively]. This clearly indicated that the green product is a copper–dibenzoylmethane salt. Elemental analysis confirmed that its chemical composition was $Cu[CH(COPh)_2]_2$. X-Ray photoelectron spectroscopy (XPS) measurements were made both for the thin film of adsorbate on copper foil and for the powder reaction product. In both cases the copper oxidation state is easily distinguished qualitatively by satellite peaks as II.

Other β-carbonyl compounds such as acetylacetone (Hacac) and ethyl acetoacetate were found to react with copper metal under mild conditions. A chemically cleaned copper plate was immersed in Hacac with vigorous agitation at ambient temperature until the liquid became dark yellow. After standing for 3 d, blue crystals were formed on the copper plate. In the case of ethyl acetoacetate, the reactant became green and bright green crystals appeared after standing for 3 d. The principal infrared

Table 1 Principal IR absorption bands (2000–400 cm^{-1}) *

Hacac	Cu + Hacac reaction product	Ethyl acetoacetate	Cu + ethyl acetoacetate reaction product	Vibration mode
1792s	1578vs	1745s	1600(br),s	C=O stretch
1709s		1718s		C=O stretch
1623m				C=O stretch
	1552s		1552s	$C\cdots O$ + $C\cdots C$ stretch
1249m		1267m		CH_2 wag
957m		930w		OH–O wag
	783s		777s	=CH wag
	455s		490s	Cu–O stretch + $C–CH_3$ def.
	431w		453w	Ring def.

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

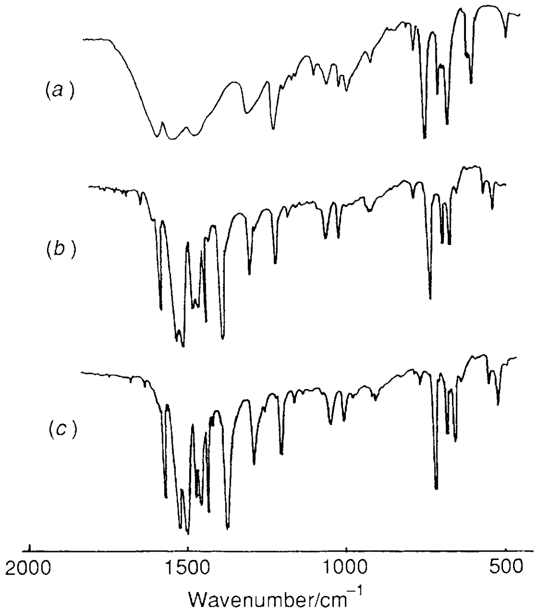


Fig. 2 Infrared spectra of the reaction of dibenzoylmethane with copper powder: (*a*) neat dibenzoylmethane; (*b*) the reaction product of copper powder with dibenzoylmethane; and (*c*) commercial copper–dibenzoylmethane salt

bands of the organic compounds and their reaction products with metallic copper are listed in Table 1.

The C=O stretching vibration bands of Hacac in the region 1709–1728 cm^{-1} are doublets, due to tautomerism. The band at 1623 cm^{-1} is due to a conjugation effect.[8] These bands were replaced by two strong bands at 1578 and 1533 cm^{-1} in the spectrum of the reaction product of Hacac and metallic copper. At the same time, the wagging vibration of $O–H\cdots O$ at 957 cm^{-1} (ref. 9) in the spectrum of Hacac disappeared in the spectrum of the reaction product, implying that one of the active hydrogen atoms of the methylene group had taken part in the reaction. The new bands at 685, 613 and 431 cm^{-1} in the spectrum of the product can be attributed to bonding of the copper cation with the acac anion.

The IR study disclosed the formation of bis(acetylacetato)-copper(II), which is usually synthesised[10] through either of the reactions (1) or (2). Our investigation indicates that copper(0)

$$2Hacac + Cu(O_2CMe)_2 \xrightarrow{OH^-} [Cu(acac)_2] \qquad (1)$$

$$2Hacac + CuO \xrightarrow{NH_3\cdot H_2O} [Cu(acac)_2] \qquad (2)$$

can react directly with Hacac at neutral pH in the presence of oxygen.

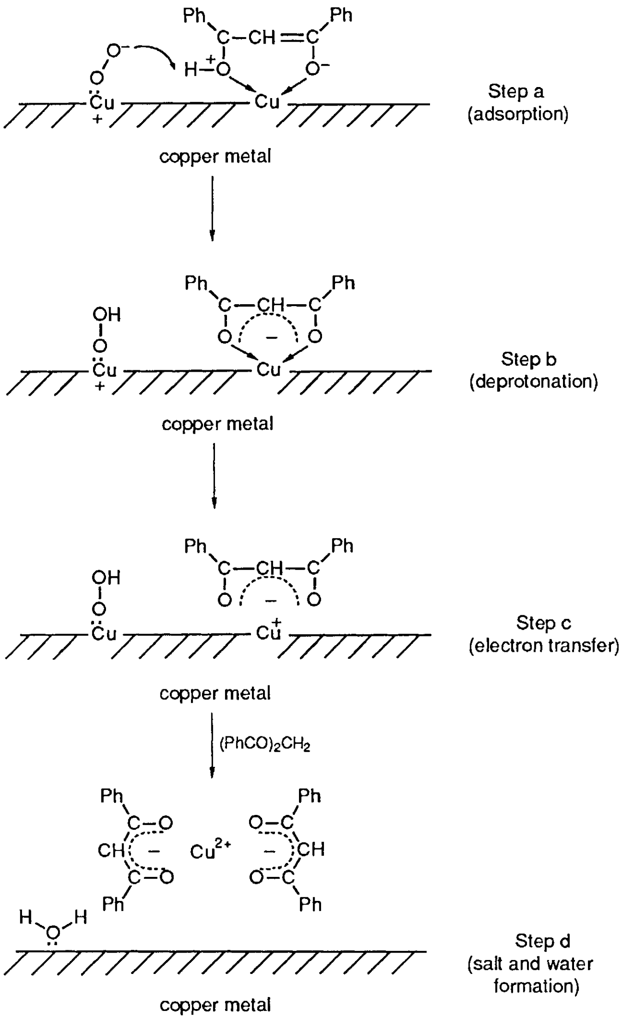
Infrared analysis of ethyl acetoacetate illustrates that a similar salt of bis(ethyl acetoacetato)copper(II) was obtained. Here, we had expected copper(II) acetoacetate to be formed in the light of Madix's acid–base model. However, deprotonation at the methylene group dominates the reaction. In order to ascertain the role of copper oxides in the reaction, powdered copper-(II) and -(I) oxides were suspended in ethyl acetoacetate with stirring for 1 week. Infrared spectroscopic study of the treated solids shows no difference from the untreated oxides, indicating that the oxide oxygen cannot remove the active hydrogen of the methylene group in ethyl acetoacetate under neutral conditions.

Acetylacetone is widely used as a corrosion inhibitor for zinc, iron and nickel in material engineering.[11] Our study on its reaction with transition metals is helpful in understanding the anticorrosion mechanism. A prevalent notion was that Hacac formed adsorbed metal acetylacetonate, which decomposed to metal oxides and species containing metal–carbon bonds, and that the decomposition was inhibited by preoxidising metals, in which case the metal acetylacetonate was formed by the reaction of the enolic proton of Hacac with the oxide oxygen.[12] We conclude that it is the oxygen chemisorbed on the metals which removes the enolic proton of the adsorbed Hacac.

Copper has long been used as a coinage metal together with silver and gold because of its resistance to corrosion under ordinary atmospheric conditions. Although the present β-diketone compounds can be deprotonated by alkali metals, copper metal has not been considered reactive enough to substitute for the methylene hydrogen of a β-dicarbonyl compound at room temperature. These unusual reactions of metallic copper in neutral, non-corrosive, organic solutions consisting of these common chemical compounds under extremely mild conditions seem to follow a new reaction scheme. We detected a minute quantity of water after these reactions when predried starting materials were used. As the oxygen was removed from the system by bubbling with prepurified nitrogen, these reactions ceased. On the basis of the reaction conditions and the structural properties of the product, we propose that reaction with dibenzoylmethane occurs on the surface according to Scheme 1.

In step b the dioxygen coadsorbed on the copper surface reacts as a strong Brönsted base to form hydroxyl groups, and subsequently, water, while charge transfer may be undertaken through the metal substrate. The range of species which react as Brönsted acids with surface oxygen extends to very weak acids; for example, benzyl cyanide ($pK_a = 26$) has been observed to react with adsorbed oxygen to form CuCN and carboxyl fragments.[13]

Due to the high basicity of adsorbed oxygen atoms, the facile extraction of protons by surface oxygen suggests that such processes may be important in hydrocarbon combustion on metal surfaces and other metal-catalysed oxidation reactions. With regard to the so-called 'Co-ordination Dual Activation



Scheme 1

Effect',[1–4,13] we have discovered many new surface co-ordination reactions of zerovalent metals with polar organic compounds which will be reported elsewhere.

Conclusion

We have shown that oxygen atoms chemisorbed on copper surfaces react as strong Brönsted bases with Brönsted acids, *i.e.* dibenzoylmethane, acetylacetone and ethyl acetoacetate. To explain the phenomenon, we have established the concept of 'Co-ordination Dual Activation Effect', and elucidated the corrosion inhibition mechanism of acetylacetone.[13]

Experimental

Preparation.—The copper disc was made from 99.99% pure copper obtained from Aldrich. It was washed with acetone, and chemically etched in 2 mol dm^{-3} HNO_3 solution at room temperature for about 4 min. This procedure removes surface oxides and creates a rough sponge-type surface with features on the 10–100 nm scale.[14,15] After the etching, the copper disc was thoroughly rinsed with water, dried with nitrogen and coated with dibenzoylmethane–ethanol solution (2% in concentration) at 50 °C for 10 min. After the physisorbed material had been removed by washing with ethanol the sample was ready for the surface-enhanced Raman scattering measurement.

Copper powder was etched with 2% HNO_3 to remove surface oxides, and was rinsed to neutral pH. A 1 g amount of the powder was then immersed in dibenzoylmethane–ethanol solution (5% in concentration, 50 cm^3) with vigorous agitation at 50 °C for 5 h. It was then exposed to air. After separation, 6 g of green solid $Cu[CH(COPh)_2]$ were obtained (Found: C, 71.00; H, 4.00; Cu, 12.80. $C_{30}H_{22}CuO_4$ requires C, 70.60; H, 4.30; Cu, 12.55%).

Chemically cleaned copper sheets (6.0 g) were immersed in Hacac (50 cm^3) with vigorous agitation at ambient temperature until the liquid became dark yellow. After standing for 3 d, blue crystals were formed on the copper sheets. The product $[Cu(acac)_2]$ was washed with ethanol and dried in vacuum at 50 °C (Found: C, 45.50; H, 5.50; Cu, 24.95. $C_{10}H_{14}CuO_4$ requires C, 45.80; H, 5.45; Cu, 24.45%). The reaction of ethyl acetoacetate and copper metal was performed in a similar way. Bright green crystals of $[Cu(MeCOCHCO_2Et)_2]$ (Found: C, 44.75; H, 5.65. $C_{12}H_{18}CuO_6$ requires C, 44.70; H, 5.60%). Differential thermal analysis showed that this salt decomposed at 193 °C, in accordance with the literature.[16]

Physical Measurements.—The surface-enhanced Raman scattering spectrum of dibenzoylmethane-treated copper was measured by the use of a Spex 1403 Raman spectrometer. The incident laser excitation was with the 5154 Å line from an argon-ion laser, and the incident power was 100 mW. Infrared spectra were obtained with a Nicolet 170 SX spectrometer; the principal bonds are shown in Table 1. X-Ray photoelectron spectroscopy indicated the binding energy of Cu(2p) in the reaction products to be 935.1 eV (*ca.* 1.5 × 10^{-16} J), suggestive of Cu^{2+}.

Acknowledgements

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