

On the mechanism of the copper(II) catalysis of the formation of urethanes from alcohols and isocyanates

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Abstract

The ability of a range of copper(II) complexes to catalyse the formation of a urethane from butanol and phenyl isocyanate in chloroform at 25°C has been investigated. Nine of the complexes were of β -dicarbonyl compounds, $\text{RCOCH}_2\text{COR}'$, where R = alkyl, and R' = alkyl or O-alkyl, and it was found that the catalytic activity of these complexes increases as the electron-donating properties of the R and R' groups increases. It is shown that this is consistent with the active species in the catalytic cycle being the dimeric copper(II) alkoxide which is formed by alcoholysis of the starting complex, and whose structure is directly analogous to that of the alkoxide which has been proposed as the active species in the tin(IV)-catalysed formation of urethanes. Further support for the catalytic role of this copper alkoxide is provided by the very high catalytic activity of the alkoxide prepared from the most active of the β -dicarbonyl complexes, i.e. that of dipivaloylmethane, and of a cationic methoxy-bridged bis(bipyridyl) complex. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Urethane; Copper catalysis; Binuclear alkoxides

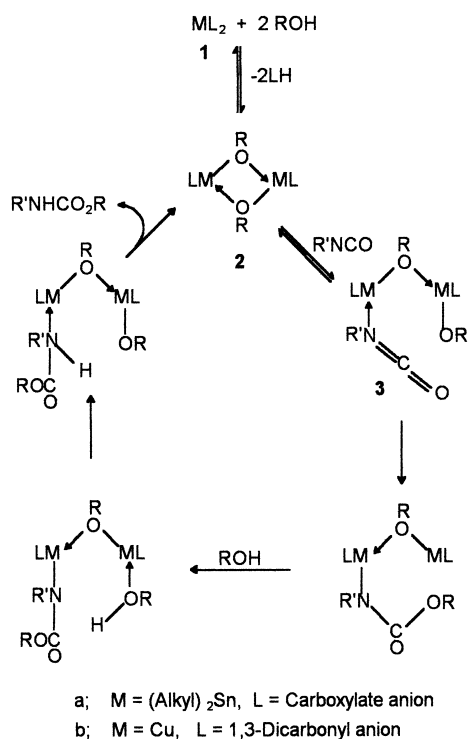
1. Introduction

The formation of urethanes from alcohols and isocyanates is catalysed by numerous inorganic compounds [1]. Dialkyltin diesters **1a** [2] and distannoxanes [3,4] are particularly effective, and dibutyltin dilaurate is widely used in the industrial preparation of polyurethanes. We have suggested [4,5] a reaction cycle (see Scheme 1) which accounts for the catalytic action of both types of tin compound and which, with the tin diesters, is initiated by alcoholysis and the formation of a tin alkoxide. This alcoholysis step was first suggested as the initial step in the catalytic cycle by Davies and Bloodworth [6], but while these authors formulated the resultant alkoxide as being

monomeric, we believe that it is the dimeric form **2a** which is the active catalyst.

As indicated in Scheme 1, the dimer **2a** can react with isocyanate to give a ring-opened product **3a** in which the co-ordinated, and therefore, activated isocyanate group can be attacked intramolecularly by the adjacent nucleophilic alkoxy group. Evidence for the involvement of an iron(III) analogue of **3a** in the catalysis of urethane formation by oxo-bridged di-iron complexes has been presented [7], and other binuclear systems similar to **3a** in which one metal activates an electrophilic substrate while another delivers a nucleophile have been established as intermediates in a number of reactions including the palladium(II), cobalt(III), and iron(III) catalysed hydrolysis of nitriles [8–11], and the zinc catalysed hydrolysis of phosphate esters [8,12].

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Scheme 1. Proposed mechanism for the copper(II)- and tin(IV)-catalysed formation of urethanes.

It has been suggested that the catalysis of urethane formation by compounds of metals other than tin is also initiated by the formation of binuclear bridged alkoxides [7], and evidence is now presented which supports this idea when the catalyst is the copper(II) complex **4** of a β -dicarbonyl compound.

2. Experimental

2.1. General

¹H and ¹³C NMR spectra were recorded for solutions in CDCl₃ on a Bruker Fourier Transform RPX 400 spectrometer operating at 400 MHz for ¹H and at 100 MHz for ¹³C, and with tetramethylsilane as an internal reference. Infrared spectra were recorded on a Perkin Elmer 1600 FTIR spectrophotometer for solutions in CHCl₃ or CH₂Cl₂, Nujol mulls (complexes) or liquid films (ligands). Mass spectra (EI) were recorded on a Fisons VG Platform II spectrometer. Micro-

analyses were performed on a Perkin Elmer 240C Elemental Analyser.

Phenyl isocyanate and butanol (HPLC grade; water <0.03%) were obtained from Aldrich and were used as received.

2.2. Ligands

The parent ligands of the complexes, **4c**, **4d** and **4e**, were prepared as described in the literature [13,14], while those of **4f** and **4g** were purchased (Aldrich) and fractionally distilled before use. The parent ligand of complex **4h** was prepared as follows:

Di-isopropylamine (1.8 ml) was added with stirring over 2 min to a solution of butyl lithium (5.44 ml; 2.3 M in hexanes) at 0°C. The hexane was removed under vacuum and the residue was dissolved in dry tetrahydrofuran (12.5 ml). The solution was cooled to -78°C and *tert*-butyl trimethylsilylacetate [15] (2.75 ml) was added dropwise with stirring over 2 min. After a further 10 min of stirring, a solution of *N*-trimethylacetylimidazole [16] (1.9 g) in dry tetrahydrofuran (12.5 ml) was added dropwise. The resultant dark orange solution was stirred for 1 h and then allowed to warm to room temperature. The mixture was quenched with hydrochloric acid (12.5 ml, 3 M), petroleum ether (50 ml) was added, and the organic layer was separated, washed with water and dried (MgSO₄). The solvent was removed under vacuum to give the crude β -ketoester (2.16 g, 94%) as a yellow oil, IR: 3635, 3399, 1736, 1709 and 1618 cm⁻¹. ¹H NMR: 1.04 (9 H, s, COCMe₃), 1.34 (9 H, s, OCMe₃), 3.31 (2 H, s, COCH₂CO). ¹³C NMR: 26.1, 28.0, 45.2, 81.6, 167.1, 208.8. This oil was used without further purification for the preparation of the complex **4h** as described later.

The replacement of *N*-trimethylacetylimidazole in the above preparation by *N*-(1-adamantylcarbonyl)imidazole afforded the parent ligand of complex **4i** as a yellow oil. Infrared spectrum: 3392, 1731, 1704, 1641 and 1616 cm⁻¹. Mass spectrum: 279 (M⁺ + 1, 30%), 205 (73), 180 (58), 164 (86), 147 (30), 114 (82), 99 (40), 85 (64), 75 (46), 63 (66); ¹H NMR 1.34 (9 H, t, J 1.8, OC(CH₃)₃), 1.50–1.96 (15 H, m, Ad-H), 3.30 (2 H, s, CH₂). ¹³C NMR: 29.5, 37.8, 39.2, 40.1, 46.8, 69.1, 82.7, 168.4, 209.5. Elemental analysis % found (calculated for C₁₇H₂₆O₃), C: 73.23 (73.35), H: 9.28 (9.41).

2.3. Copper(II) complexes

Complexes **4a** and **4b** were purchased (Aldrich) and purified by crystallisation from chloroform. Complexes **4, c–i**, were prepared by the action of copper(II) acetate on the parent ligand. With **4c, 4d** and **4e**, the presence of a base was not required, but on account of the reduced acidity of the parent ligands the preparation of **4f** and of **4g, 4h** and **4i**, required the use of triethylamine and sodium hydroxide, respectively.

Bis(methyl 3-oxobutanoato)copper(II), **4f**. The parent β -keto ester (5.0 g) in methanol (30 ml) followed by triethylamine (3.89 g) in methanol (10 ml) was added with stirring to a warm solution of copper(II) acetate monohydrate (3.84 g) in water (100 ml). The resultant green precipitate was filtered off, washed with ether, and recrystallised from chloroform to give the complex (4.86 g, 77%) as green needles. Infrared spectrum: 1600 and 1536 cm^{-1} . Elemental analysis % found (calculated for $\text{C}_{10}\text{H}_{14}\text{CuO}_6$): C: 40.62 (40.89), H: 4.88 (4.77). The complexes, **4c, 4d** and **4e**, all of which have been reported previously, were prepared in a similar manner except that the triethylamine was omitted. Yields (%), melting points ($^{\circ}\text{C}$), and literature melting points were as follows: **4c**, 28, 209–211, 209–210 [13]; **4d**, 30, 126–128, 127–129 [17]; **4e**, 64, 196–197, 197–198 [13].

Bis(ethyl 3-oxopentanoato)copper(II), **4g**. The parent keto ester (0.81 g) in methanol (10 ml) followed by a solution of sodium hydroxide (0.2261 g) in methanol (10 ml) was added with stirring to a warm solution of copper(II) acetate monohydrate (0.56 g) in methanol (30 ml). The resultant precipitate of sodium acetate was filtered off and washed with chloroform. The filtrate and washings were combined, the solvent was removed under vacuum and the residue was recrystallised from ether to give the complex (0.68 g, 69%) as green crystals, mp 146–147 $^{\circ}\text{C}$ ([18] 146–147 $^{\circ}\text{C}$); Infrared spectrum: 1595 and 1523 cm^{-1} . Elemental analysis % found (calculated for $\text{C}_{14}\text{H}_{22}\text{CuO}_6$), C: 48.21 (48.06), H: 5.99 (6.34).

Complex **4h** was prepared in an identical manner (61% yield) and after crystallisation from dichloromethane/acetone had mp 229–230 $^{\circ}\text{C}$. Infrared spectrum: 1597, 1578, 1532 and 1506 cm^{-1} ; Mass spectrum: 462 (M^+ , 7%), 349 (32), 292 (30), 235 (31), 149 (37), 127 (32), 87 (77), 85 (43), 69 (53), 59 (63), 56(100). Elemental analysis % found

(calculated for $\text{C}_{22}\text{H}_{38}\text{CuO}_6$), C: 57.00 (57.18), H: 8.42 (8.29).

Complex **4i** was prepared similarly (58% yield), and had mp 236–237 $^{\circ}\text{C}$. Infrared spectrum: 1588, 1571 and 1509 cm^{-1} ; Mass spectrum: 618 (M^+ , 3%), 506 (16), 460 (18), 222 (54), 135 (100), 107 (50), 93 (90), 79 (91), 59 (74), 56 (83). Elemental analysis % found (calculated for $\text{C}_{34}\text{H}_{50}\text{CuO}_6$), C: 66.18 (66.05), H: 7.89 (8.15).

Preparation of the tetramer **6e**. The procedure used by Berke and coworkers [19] to prepare the tetramer **6c** was followed exactly, except that the 2-methoxyethanol was replaced by ethanol. This afforded the complex (66% yield) as a light blue microcrystalline solid, mp 216–217 $^{\circ}\text{C}$. Infrared spectrum: 1586, 1568 and 1530 cm^{-1} . Elemental analysis % found (calculated for $(\text{C}_{13}\text{H}_{24}\text{CuO}_3)_4$), C: 53.50 (53.50), H: 7.96 (8.29).

2.4. Experimental procedures

Solutions containing phenyl isocyanate (0.15 M), butanol (0.15 M) and the copper catalyst (0.001 M) were prepared in spectrophotometric grade chloroform (Aldrich) which had been stored over type 4 Å molecular sieves. Formation of the urethane at 25 $^{\circ}\text{C}$ was followed by measuring the absorbance of the infrared band which developed at 1731 cm^{-1} . With a urethane concentration within the range 0–0.2 M, the absorbance of this band bears a linear relationship to urethane concentration, and the infrared spectra of the reaction mixtures showed that, in all cases, urethane was the only product. In order to determine the $t_{1/2}$ value for a specific complex, infrared spectra (each with four scans) were recorded at appropriate intervals, the lengths of which were determined by the activity of the complex. With **4b** and **4e**, for example, spectra were recorded every 3 h and every 10 min, respectively. The value of $t_{1/2}$ was then taken from a graphical plot of absorbance against time.

In order to investigate the catalytic activity of **7a**, the hexafluorophosphate salt of this cation was prepared as described by Perlepes et al. [20], and a suspension of this salt (18.3 mg), sodium tetraphenylborate (8.55 mg) and dichloromethane (25 ml) was stirred magnetically for 18 h by which time all the salt had been solubilised. The resultant solution was used to prepare 0.30 M solutions of phenyl isocyanate and

of butanol which were mixed immediately. Urethane formation was then followed as indicated above, for it has been established [7] that in dichloromethane also, the absorbance of the infrared band at 1731 cm^{-1} bears a linear relationship to urethane concentration.

3. Results and discussion

In the absence of a catalyst, the reaction between equimolar amounts (0.15 M) of butanol and phenyl isocyanate in chloroform at 25°C is quite slow, and the time taken for it to reach the halfway stage ($t_{1/2}$) is about 40 h. This length of time is reduced significantly (see Table 1) when the copper(II) complexes **4** of various β -diketones and β -keto esters are incorporated (0.001 M) into the reaction mixture, thus confirming observations by earlier workers [21–25] that complexes of this type catalyse urethane formation.

The data in Table 1 indicate that the catalytic activity of the complexes is very dependent on two groups, R and R', which flank the dicarbonyl system, and two general trends are immediately obvious. The first is that the progressive methylation of the four methyl groups in the simplest of the β -diketone and β -keto ester complexes, i.e. **4b** and **4f** respectively, causes a progressive increase in catalytic activity. The activity of the β -diketone complexes, **4b**, **4c**, **4d** and **4e**, for example, increases in that order, with the last complex being a very effective catalyst for the reaction. The second trend is that complexes of β -keto esters are usually more active than those of the corresponding

β -diketones, as with **4f** and **4b**, and **4g** and **4c**, although this trend does not apply to the pair **4h** and, the most active of all the complexes, **4e**.

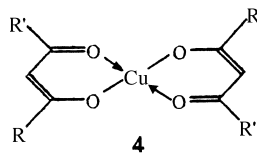
Before offering a mechanistic explanation for these two trends it is necessary to comment on a suggestion [21,25] that catalysis of urethane formation by the acetylacetonate complex **4b** involves, in part, the isocyanate being activated by co-ordination with the copper ion through its nitrogen and oxygen atoms. While the suggestion that co-ordination results in activation is a realistic one, co-ordination can involve only the nitrogen or the oxygen atom, but not both atoms at the same time. The stereochemical arrangement of the lone pairs on these two atoms does not permit an isocyanate to act as a bidentate ligand for copper(II).

The activity of **4b** and, indeed, the relative activities of all the complexes listed in Table 1, can be more convincingly explained if it is assumed that the catalytic cycle for urethane formation involves not the starting complex itself, but rather the dimeric alkoxide **5** that is formed by alcoholysis (see Scheme 2), i.e. the copper(II) analogue of the dimer **2a** which has been proposed as the active catalyst in the tin(IV) system.

As with most ligand substitutions the alcoholysis of copper bis(β -diketonates) is reversible, but in 1964 Bertrand and Caine demonstrated that the reaction can be used to obtain preparative yields of alkoxy copper β -diketonates if a base, preferably an alkoxide of the alcohol, is incorporated into the reaction mixture [26]. Presumably, the function of this base is to remove the weakly acidic β -diketone from the equilibrium, thereby displacing the equilibrium to the right hand side. Since then, many alkoxy copper β -diketonates have been prepared by this method, largely in attempts to obtain compounds which might be converted into semi-conducting ceramic materials by the *sol-gel* process [27]. X-ray solid-state structures for a number of these alkoxides have been determined, and in all cases it has been established that these compounds contain the dimeric unit **5** (see the recent and very extensive review by Melník and co-authors [28] on oligomeric copper complexes). In a few cases this unit is the actual structure of the alkoxide, as with **5a** [29], but far more frequently encountered are the tetrameric alkoxides which contain two of the dimer units held almost parallel to each other by bonds between (usually) four pairs of copper and oxygen atoms as illustrated in structure **6**. Molecular weight determinations [19] indicate

Table 1

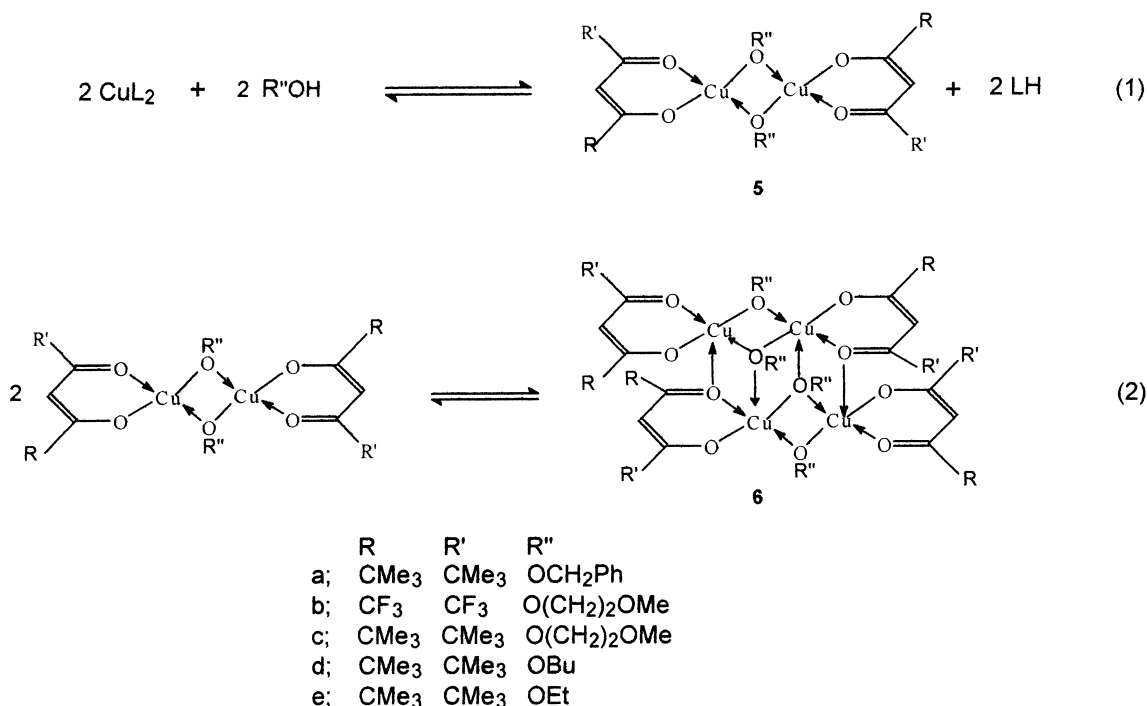
Time ($t_{1/2}$) taken for the copper(II) catalysed reaction between butanol and phenyl isocyanate in chloroform at 25°C to be 50% complete



Complex	4a	4b	4c	4d	4e	4f	4g	4h	4i
R	CF ₃	Me	Et	Pr ⁱ	Bu ^t	Me	Et	Bu ^t	1-Ad ^a
R'	CF ₃	Me	Et	Pr ⁱ	Bu ^t	OMe	OEt	OBu ^t	O-Bu ^t
$t_{1/2}$ (h)	20	16.5	8.0	2.5	0.8	4.0	1.8	1.6	1.2

^a 1-Ad = 1-adamantyl.

Concentrations: butanol and isocyanate, 0.15 M; catalyst, 0.001 M.



Scheme 2. Formation of dimeric and tetrameric alkoxides by the alcoholysis of the copper(II) complex of a β -dicarbonyl compound.

that in chloroform these tetrameric alkoxides exist in equilibrium with the dimeric form **5** (Scheme 2).

Molecular models show that when the ring in one of the dimer units of a tetrameric copper alkoxide is opened by isocyanate in the manner illustrated for the dimer **2b** in Scheme 1, the changes in bond angles and in the relative position of the two copper atoms in that unit require at least two of the inter-dimer copper–oxygen bonds to be broken. Ring-opening by isocyanate will therefore proceed more slowly than with the dimeric form of the alkoxide. Because of this, it is the dimeric form of the alkoxide which is the more important active species in the catalytic cycle, and it is demonstrated below that it is the extent to which this species is formed by alcoholysis that determines the relative catalytic activity of copper complexes of type **4** in urethane formation.

In the absence of an added base and for a series of directly related ligands, the main factor that determines the extent of the alcoholysis shown in equation (1) is the acidity of the β -dicarbonyl compound LH. As this decreases, the equilibrium is displaced to

the right-hand side and the concentration of alkoxide increases. While no $\text{p}K_{\text{a}}$ data for β -dicarbonyl compounds appear to have been reported for solutions in chloroform, relative acidities in that solvent can be deduced from other published data. For example, several studies [30–33] using a range of solvents have shown consistently that the acidity of diketones, RCOCH_2COR , decreases in the order $\text{R} = \text{CF}_3 \gg \text{Me} > \text{Et} > \text{CHMe}_2 > \text{CMe}_3$, i.e. as the electron-releasing properties of the R groups increase. From this it follows that of the five β -diketone complexes listed in Table 1, it is **4a** which will afford the lowest concentration of a copper alkoxide on alcoholysis, and **4e** the highest.

The alkoxide formed from **4a** will, however, show only a low tendency to exist in the catalytically active dimeric form **5**, for the molecular weight determinations which have been carried out on tetrameric alkoxides **6** in chloroform show that if the R and R' groups are CF_3 the tetrameric form is stabilised quite substantially with respect to dissociation [19,34]. Clearly, a combination of this stabilisation and the relatively

high acidity of hexafluoroacetylacetone, pK_a 6.0 in 75% aqueous dioxan [33], will ensure that **4a** gives only a low concentration of dimeric alkoxide on alcoholysis, and this in turn will result in **4a** being a poor catalyst in urethane formation.

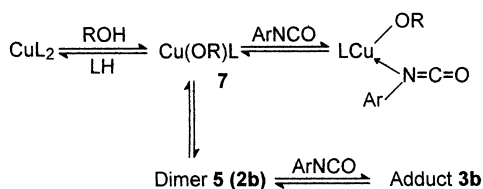
Conversely, with the other four β -diketone complexes, the order **4b** < **4c** < **4d** < **4e** almost certainly reflects not only the extent to which these complexes undergo alcoholysis, but also the extent to which the resultant alkoxides exist in the dimeric form **5**. This is because as one passes along the series, R and R' = Me, Et, CHMe₂, CMe₃, the size of these alkyl groups, as well as their electron-donating properties, increases. This increase will lead to a decrease in the stability of the tetrameric form of the alkoxide, for the two dimer units in the tetramer lie almost parallel to each other, and as the size of the R and R' groups increases so also do the steric interactions which arise between the groups that are in one unit and those parts of the other unit which are immediately adjacent. These interactions have been shown [29,35] to be particularly pronounced when R = R' = *tert*-Bu, and, as a result, of the four β -diketone complexes, **4, b–e**, it is the last which gives the highest overall concentration of dimeric alkoxide and is therefore the most active urethane-forming catalyst. In this connection, it should be noted that while the complex **6b** with its trifluoromethyl groups retains the tetrameric structure in chloroform, the *tert*-butyl analogue **6c** dissociates to the dimeric form **5c** to an extent of nearly 90% [19]. This difference is, of course, very relevant to the marked contrast between the catalytic activities of **4a** and **4e**.

Because of resonance stabilisation of the ester group, β -keto esters are less acidic and weaker chelating agents than the corresponding β -diketones, and both these characteristics will result in the extent of alcoholysis of the complexes **4f**, **4g**, and **4h**, being significantly greater than with the corresponding β -diketone complexes **4b**, **4c**, and **4e**. With the copper alkoxide formed from a β -keto ester complex, however, the steric interactions which destabilise the tetrameric form are probably not as great as those present in the corresponding β -diketone alkoxide. This is because rotation about the carbon–oxygen bonds in the two ester groups (CO–O alkyl) in each of the dimer units will allow the ester alkyl groups in both units to point away from those parts of the

other unit that are immediately adjacent. With the two β -keto ester complexes **4f** and **4g**, it would appear that the higher degree of alcoholysis more than compensates for the lower tendency of the resultant alkoxides to exist in the dimeric form, for both these complexes are significantly more active catalytically than the corresponding diketone complexes **4b** and **4c**. With **4h**, however, this is not the case, and even though it would be expected to undergo alcoholysis to a greater extent than the corresponding diketone complex **4e**, it is the latter complex which generates an overall higher concentration of active dimeric alkoxide because of the very large steric interactions which destabilise the tetrameric form. Significantly, the diketone complex **4e** is also more active than **4i** with its bulky 1-adamantyl groups.

In our urethane-forming system the alcohol is butanol. The dimeric alkoxide generated from the most active complex, **4e**, is therefore **5d** which, by analogy with the isosteric methoxyethoxy alkoxide **5c** [19,36], would probably have the tetrameric structure **6d** in the solid state. Berke and co-workers [19] obtained **6c** by using the general method devised by Bertrand and Caine, i.e. by treatment of **4e** with the appropriate sodium alkoxide. Although we were unable to obtain a pure sample of **6d** by this approach, use of sodium ethoxide afforded an analytically pure sample of the ethoxy analogue **6e**. When this complex was used as the urethane-forming catalyst and at the same copper concentration used for the complexes **4, a–i**, the reaction had a $t_{1/2}$ value of only 32 min. Although the presence of the ethoxy groups in the complex do not allow a direct comparison of this value with that (50 min) of the parent complex **4e**, one would expect that the catalytic cycle for urethane formation would cause the ethoxy derivative **6e** to be rapidly converted into the butoxy derivative **6d**. On this basis, a comparison of the two $t_{1/2}$ values indicates that under the conditions of urethane formation, i.e. a copper to alcohol ratio of 1:150, the alcoholysis of the parent complex **4e** occurs to a very substantial extent.

A high degree of alcoholysis was also indicated by the data obtained from kinetic runs using different concentrations of the complex **4e** to catalyse urethane formation. These runs were carried out largely in order to eliminate the possibility that the active catalyst in the urethane-forming reactions was the monomeric alkoxide **7** (see Scheme 3), rather than its dimeric form



Scheme 3. The reaction of isocyanate with the monomeric and the dimeric forms of the copper alkoxide.

5. This monomer is, of course, the initial product of alcoholysis, but because it is co-ordinatively unsaturated it would be expected to dimerise very rapidly.

Using the usual conditions, $t_{1/2}$ values were measured using the complex **4e** at concentrations in the range 2.5×10^{-4} – $4.0 \times 10^{-3} \text{ mol l}^{-1}$. It was found that only at the lowest concentration did a plot of $t_{1/2}$ against the reciprocal of complex concentration deviate from the straight line required by the relationship $t_{1/2} = (\ln 2)/k[c]$, where k is the pseudo first-order rate constant for the reaction between the isocyanate and a copper alkoxide whose concentration $[c]$ remains effectively constant up to the point where half of the isocyanate and the alcohol have reacted (see Fig. 1). In order for the concentration of the alkoxide to be independent of alcohol concentration over the period

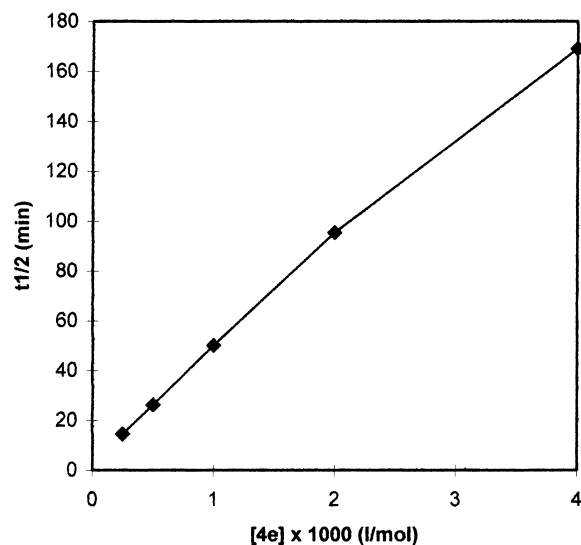
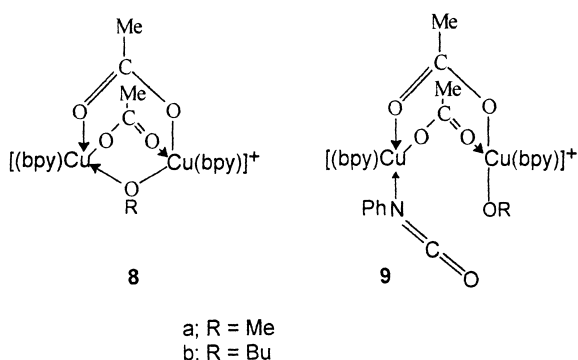


Fig. 1. Effect of the concentration of the complex **4e** on the time taken for the reaction between phenyl isocyanate and butanol (both 0.15 M) in chloroform at 25°C to be 50% complete.

in which the latter is halved, the starting complex **4e** must undergo virtually complete alcoholysis at all the alcohol concentrations involved. Also, for the relationship given above to apply, the alkoxide which reacts with the isocyanate must be either the dimer **5e** or the corresponding monomer of type **7**, but not a mixture of both, for the relative amounts of the two alkoxides in such a mixture would be dependent upon the concentration of **4e**. Bearing in mind the rapidity with which the monomer would be expected to dimerize, it is extremely unlikely that only this form would be formed on alcoholysis, and the data therefore appear to rule out the possibility that it is the monomeric alkoxide, rather than the dimeric form, which is the active catalyst. We believe that a far more detailed kinetic study would confirm this point. In this connection we note that a great deal of very careful kinetic work has been carried out on the tin(IV)-catalysis of urethane formation, most notably and recently by Tondeur and co-workers [37–40]. Unfortunately, it would appear that, with none of the systems investigated, was an attempt made to establish whether or not the data obtained were consistent with the suggestion [4] that the catalytic cycle proceeds largely through the dimeric tin alkoxide **2a**.



Finally, further support for the proposed high catalytic activity of binuclear copper alkoxides was obtained by a study of the bridged bipyridyl (bpy) cation **8a**, which was prepared as its hexafluorophosphate salt [20]. Although this salt proved to be almost insoluble in chloroform, i.e. the solvent used to study the activity of the β -dicarbonyl complexes, it was found possible to solubilise the salt in dichloromethane by using the metathesis procedure with sodium tetra-

phenylborate used previously for di-iron complexes [7]. In the absence of any catalyst the reaction between butanol and phenyl isocyanate in dichloromethane is significantly faster than in chloroform, and a $t_{1/2}$ value of about 17 h has been reported [7] when both reactants have a concentration of 0.15 M. In the presence of the cation **8a** (0.001 M), however, this value was found to be reduced to just under 30 min, indicating very strong catalysis. We consider that this is the result of the cation reacting with isocyanate to give the ring-opened product **9a**, which then participates in a cycle directly analogous to that shown in Scheme 1 for **3b**. This cycle will catalyse not only urethane formation, but also alkoxy exchange to give **8b**.

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