Radical Cations in the Decomposition of Diphenyldiazomethane Induced by Copper Perchlorates

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Summary Kinetic and e.s.r. spectroscopic observations on the decomposition of diphenyldiazomethane in alkyl cyanide solvents induced by copper(II) perchlorate suggest that two radical cations, one derived from the diazoalkane and the other from benzophenone azine, are key intermediates in a chain process.

There is continuing interest in the mechanisms of reactions of diazoalkanes induced by copper-containing catalysts, particularly regarding the formation of copper carbenoids and the oxidation state of copper in such species.[1] We report here some results from an investigation of the mechanism of the decomposition of diphenyldiazomethane in the presence of catalytic amounts of copper(I) and copper(II) perchlorates in alkyl cyanide solutions.

Copper(I) perchlorate in acetonitrile smoothly decomposes the diazoalkane giving benzophenone azine and a little benzophenone. Addition of water to the solution has little kinetic effect but increases the proportion of benzophenone. By contrast, copper(II) perchlorate ($1{\cdot}3 \times 10^{-4}$M) on addition to diphenyldiazomethane ($1{\cdot}6 \times 10^{-2}$M) produces a transient blue colour (λ_{max} *ca.* 650 nm) followed by smooth decomposition yielding tetraphenylethylene and traces of diphenylmethanol, benzophenone and its azine, and benzpinacol.[2,3] The proportion of azine can be increased, largely at the expense of tetraphenylethylene, by the use of low concentrations of copper(II) perchlorate, high concentrations of diazoalkane, or by the use of solvents of lower dielectric constant such as heptyl cyanide, especially in the absence of oxygen.

For both copper salts in anhydrous acetonitrile, the reaction rate, $v = k\,[Ph_2CN_2][Cu]$, but $k(Cu^{II}) =$ *ca.* 300 $k(Cu^{I})$ at 30 °C. Addition of water or deuterium oxide to the copper(II)-containing reaction mixtures leads to characteristic rate changes (Figure 1) with a maximum at *ca.* 0·2M water. At higher water concentrations, the kinetics, solvent isotope effect, and products all indicate that the major reaction path involves $HClO_4$ catalysis.[4] At very low water concentrations, however, the isotope effect falls to $<$1·2 and the rate and products are then identical to those observed using the cation radical salt tris(*p*-bromophenyl)ammoniumyl perchlorate[5] instead of copper(II) perchlorate. Addition of copper(I) perchlorate retards reactions induced by the copper(II) salt and changes the kinetic form to a second-order dependence on the diazoalkane.

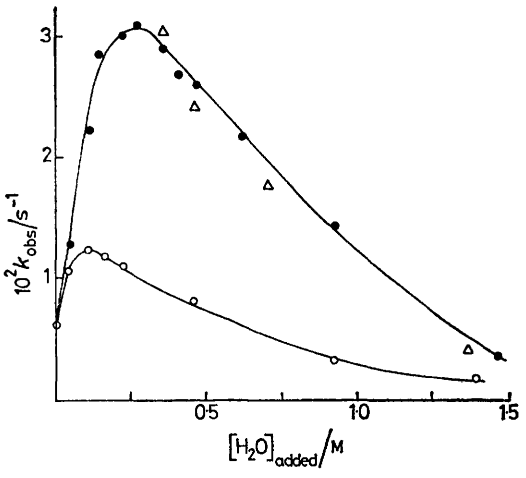

FIGURE 1. Observed velocity constants, k_{obs} (=k[catalyst]) for the disappearance of diazodiphenylmethane at 30 °C in acetonitrile containing added water: ●, $Cu(ClO_4)_2 + H_2O$; ○, $Cu(ClO_4)_2 + D_2O$; △, $HClO_4 + H_2O$. Catalyst concentration, $1·3 \times 10^{-4}$M

Under conditions similar to those of the kinetic experiments using copper(II) perchlorate but with degassed heptyl cyanide as solvent, strong e.s.r. signals were observed. In the range 20—40 °C, the spectrum (which was particularly intense at the end of the reaction) consisted of a single envelope of lines, of which at least 31 were discernible; this appears to be identical with the spectrum observed by Gaspar and his co-workers[6] and assigned to benzophenone azine radical cation. By repeating the experiment at temperatures between −60 and 0 °C the quite different spectrum shown in Figure 2, and containing five groups of seven lines, was found. On raising the temperature, it was transformed into the 31-line spectrum. We assign the low temperature spectrum to diphenyldiazomethane radical cation. Preliminary INDO calculations of hyperfine coupling constants and computer simulation of the corresponding spectrum obtained using 9-diazofluorene seem to

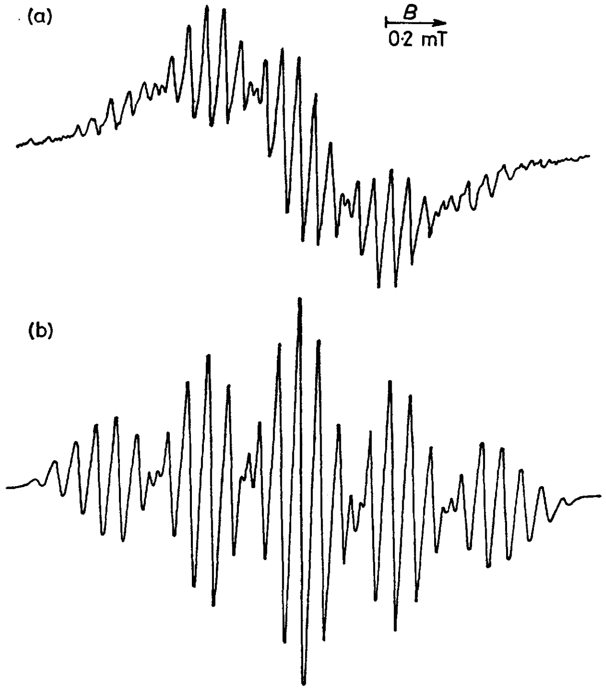

FIGURE 2. (a) The e.s.r. spectrum of a degassed solution containing diazodiphenylmethane (*ca.* 2M) and copper(II) perchlorate (10^{-2}M) in heptyl cyanide at −7 °C. (b) A computer simulation using the following hyperfine splitting constants: a_N, 0·266 (two nitrogens); a_H, 0·118 (two *p*-hydrogens); and a_H, 0·057 mT (four *o*-hydrogens). The line width was 0·027 mT. Hence $a_H < 0·005$ mT for the *m*-hydrogens.

confirm this assignment.‡ The initial blue colour is stable at −60 °C, but at the higher copper(II) perchlorate concentration required to convert all the diazoalkane into the coloured species, only very weak and unresolvable e.s.r. signals could be detected. The blue species thus does not appear to be radical. The tetraphenylethylene radical cation was not detected under the reaction conditions.

On the basis of the combined kinetic, product, and spectroscopic results, we propose the mechanistic interpretation outlined in the Scheme.[3] The radical cations are key intermediates under anhydrous conditions, and the rate-limiting step is thought to be the reaction of the

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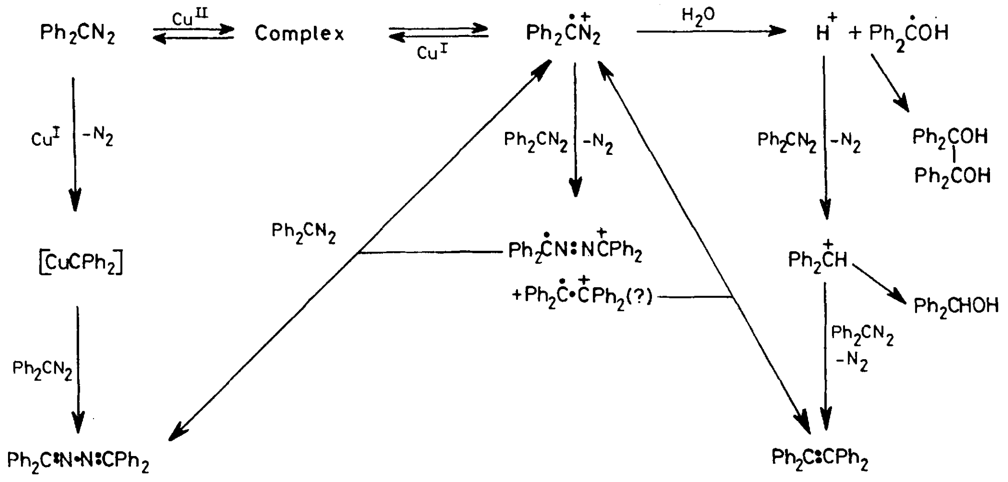
‡ For 9-diazofluorene radical cation, planar geometry was assumed except for the terminal nitrogen atom (∠C–N–N, 160°). This gave small $|a_H|$-values (0·06 to 0·24 mT) and approximately equal $|a_N|$-values (0·553 and 0·501 mT). Calculations on diazodiphenylmethane cation radical are in progress, but these are more complicated because of the larger number of possible geometries.



Scheme

diazoalkane radical ion with further diazoalkane. Added water interrupts the chain producing perchloric acid and hence diphenylmethyl cations. Copper(I) perchlorate clearly leads to a completely separate mechanistic pathway, yielding benzophenone azine presumably *via* a copper carbenoid.

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