The nature of the blue species formed when 1,1-diphenylethylene chemisorbs and reacts on acidic solids

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The blue species obtained when 1,1-diphenylethylene chemisorbs on highly acidic solids arises from a very minor dimerization reaction where a less stable canonical form of the initial carbenium ion adds to $\Phi_2C{=}CH_2$ (Φ = phenyl). Proton loss followed by H^- ion abstraction from the resulting olefin then affords a highly conjugated ion as the blue species.

Keywords: dimerization of 1,1-diphenylethylene, acidic solids and liquids, carbenium ions, role of different forms of resonance hybrids

When $\Phi_2C{=}CH_2$ is absorbed on activated silica–alumina or highly acidic zeolites, a yellow complex is first formed (λ_{max}, 423 nm) followed by the rapid development of a bright blue species (λ_{max}, 605 nm) [1]. The yellow and blue species are also formed in a variety of strong Brønsted liquid acids, e.g., concentrated sulphuric acid/glacial acetic acid mixtures [2]. Furthermore, ESR analysis [3] revealed that the silica–alumina/$\Phi_2C{=}CH_2$ system also contained a small concentration of cation-radicals. The yellow species is the carbenium ion $\Phi_2C^+{–}CH_3$ formed by protonation of $\Phi_2C{=}CH_2$, but the nature of the blue species was a puzzle and the subject of intense investigation by many groups during the past half century. It was clearly not the cation-radical [1], since the yellow species and the cation-radical are both bleached and eliminated by addition of controlled amounts of water to the silica–alumina system [4] leaving the diamagnetic (ESR check) blue species as intense as ever. Addition of excess water eventually bleaches the blue species as well. At this stage extraction of the surface by ether followed by drying and solvent removal left minute traces of a colourless solid which on addition in dry benzene solution to anhydrous $Mg(ClO_4)_2$ immediately gave back the blue species. $Mg(ClO_4)_2$ is a Lewis acid and the test is specific for the presence of indicator alcohols such as Φ_3COH [5], so the blue species is washed off the silica–alumina as an alcohol.

In sulphuric/acetic acid mixtures $\Phi_2C{=}CH_2$ also gives the yellow and blue carbenium ions, but the main catalytic reaction is dimerization via the initial carbenium ion in the canonical form $\Phi_2C^+{–}CH_3$ with the precipitation of 1,1,3,3-tetraphenylbut-1-ene in almost 100% yield (scheme 1). On silica–alumina the dimeric ion also undergoes an intramolecular alkylation reaction giving the corresponding indane product (scheme 2) [6]. All of this evidence led to the suggestion [4] that the blue species is also a dimeric ion formed from the initial one by the steps shown in scheme 3. The completely conjugated 1,1,3,3-tetraphenyl-2-methylpropenyl ion would be expected to absorb light at longer wavelengths. The final H^- ion removal step is well known [4,5] to occur for compounds of the type Φ_3CH on acidic solids. However, subsequent work in the late 1960's [7], but only briefly mentioned later in a review paper [6] showed that the idea in scheme 3 is also incorrect. We found that 1,1,3,3-tetraphenylpropene is very easily prepared by the following convenient one-step procedure [6]. When an equimolar mixture of Φ_2CHOH and $\Phi_2C{=}CH_2$ is dissolved in glacial acetic acid at 0 °C and concentrated sulphuric acid gradually added, the cross dimer, $\Phi_2CH{–}CH{=}C\Phi_2$, precipitates out quantitatively without formation of the dimer of $\Phi_2C{=}CH_2$ shown in scheme 1. Clearly Φ_2CHOH is much more easily protonated than $\Phi_2C{=}CH_2$ even though the $\Phi_2C^+{–}CH_3$ ion should be intrinsically more stable than the Φ_2CH^+ ion, so the energetics of the elimination of water in the acid makes the steps shown in scheme 4 greatly preferred. When $\Phi_2CH{–}CH{=}C\Phi_2$ is added to activated silica–alumina, a variety of species including cation-radicals are observed with the UV spectrum showing bands at 370, 417, 453, and 563 nm, but none in the 600 nm region as might have been expected if scheme 3 is correct. We then synthesized 1,1,3,3-tetraphenylpropene-3-ol by a simple Grignard reaction involving 1,1-diphenyl-2-bromoethene and benzophenone. The former compound was easily prepared [8] by bromination of $\Phi_2C{=}CH_2$ followed by dehydrobromination. Addition of 1,1,3,3-tetraphenylpropene-3-ol to silica–alumina gave a strong UV spectrum with three intense bands at 370, 453, and 563 nm, which can be assigned to the 1,1,3,3-tetraphenylpropenyl ion.

Although this work has been briefly published [6], the idea in scheme 3 as the source of the blue species has been strongly supported in a very recent review [1], with the alternative phenyl shift also suggested (scheme 5).

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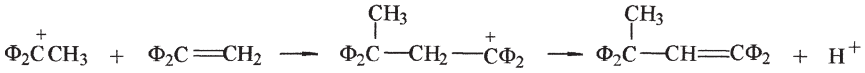
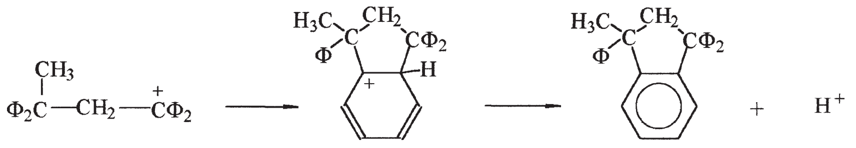
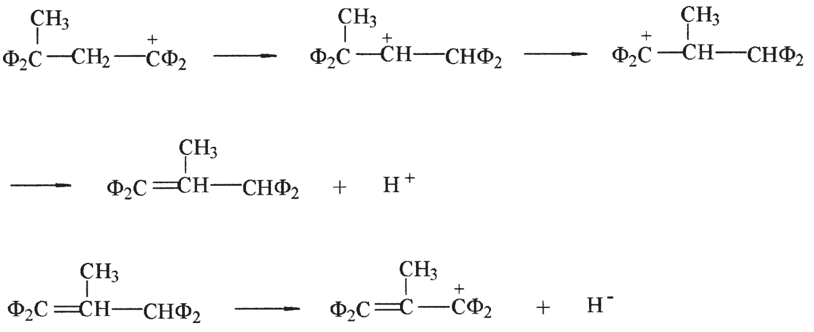


$$\Phi_2\overset{+}{C}CH_3 + \Phi_2C{=}CH_2 \rightarrow \Phi_2\overset{CH_3}{\overset{|}{C}}-CH_2-\overset{+}{C}\Phi_2 \rightarrow \Phi_2\overset{CH_3}{\overset{|}{C}}-CH{=}C\Phi_2 + H^+$$

Scheme 1.



Scheme 2.

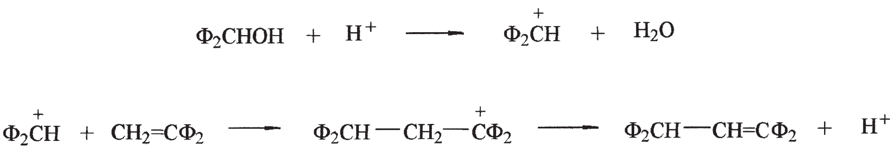


$$\Phi_2\overset{CH_3}{\overset{|}{C}}-CH_2-\overset{+}{C}\Phi_2 \rightarrow \Phi_2\overset{CH_3}{\overset{|}{C}}-\overset{+}{C}H-CH\Phi_2 \rightarrow \Phi_2\overset{+}{C}-\overset{CH_3}{\overset{|}{C}}H-CH\Phi_2$$

$$\rightarrow \Phi_2C{=}\overset{CH_3}{\overset{|}{C}}H-CH\Phi_2 + H^+$$

$$\Phi_2C{=}\overset{CH_3}{\overset{|}{C}}H-CH\Phi_2 \rightarrow \Phi_2C{=}\overset{CH_3}{\overset{|}{C}}-\overset{+}{C}\Phi_2 + H^-$$

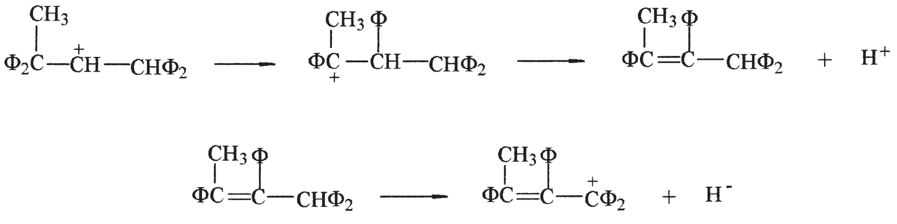
Scheme 3.



$$\Phi_2CHOH + H^+ \rightarrow \Phi_2\overset{+}{C}H + H_2O$$

$$\Phi_2\overset{+}{C}H + CH_2{=}C\Phi_2 \rightarrow \Phi_2CH-CH_2-\overset{+}{C}\Phi_2 \rightarrow \Phi_2CH-CH{=}C\Phi_2 + H^+$$

Scheme 4.



$$\Phi_2\overset{CH_3}{\overset{|}{C}}-\overset{+}{C}H-CH\Phi_2 \rightarrow \Phi\underset{+}{\overset{CH_3}{\overset{|}{C}}}-\overset{\Phi}{\overset{|}{C}}H-CH\Phi_2 \rightarrow \Phi\overset{CH_3}{\overset{|}{C}}{=}\overset{\Phi}{\overset{|}{C}}-CH\Phi_2 + H^+$$

$$\Phi\overset{CH_3}{\overset{|}{C}}{=}\overset{\Phi}{\overset{|}{C}}-CH\Phi_2 \rightarrow \Phi\overset{CH_3}{\overset{|}{C}}{=}\overset{\Phi}{\overset{|}{C}}-\overset{+}{C}\Phi_2 + H^-$$

Scheme 5.

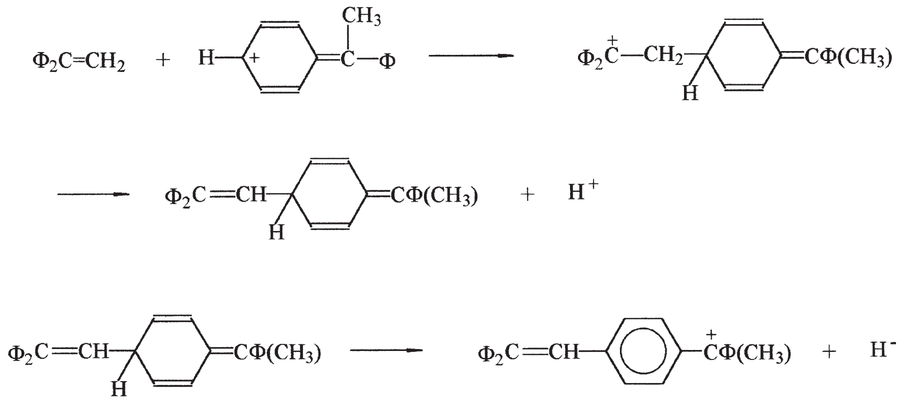
The authors [1] are obviously unaware of our evidence and also that the structure of the blue ion has been elucidated [6]. We remained puzzled for several years until it suddenly dawned on us that the representation $\Phi_3^+{-}CH_3$, of the initial ion is only one canonical form. Suppose that the dimerization ultimately affording the blue complex proceeds via the less stable canonical form, as shown in scheme 6 [7]. The final H^- ion elimination should be very rapid yielding the highly conjugated product ion as the blue species.

In order to test scheme 6, we carried out the synthesis shown in scheme 7.

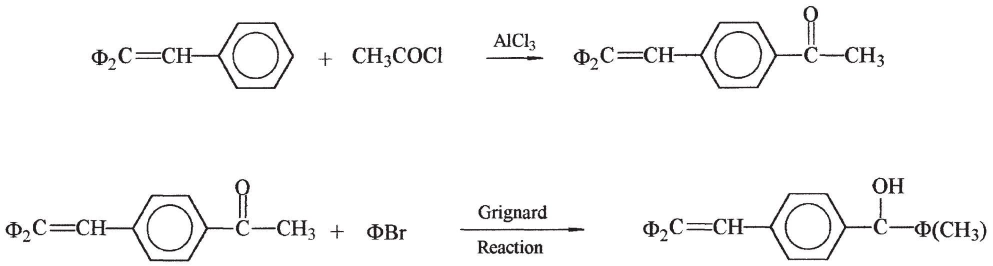
The acylation step in scheme 7 is fortunately very selective [9], so we obtained the final alcohol in good yield. When this compound is added to silica–alumina, weak liquid acids, or to anhydrous $Mg(ClO_4)_2$, the blue carbenium ion is immediately formed. This alcohol is therefore an excellent indicator for weak acids, but is not specific as it responds to both Lewis and Brønsted sites.

The chemistry reported here illustrates several important points. Thus the blue ion is a significant species from the point of view of chemisorption since it is abundant on the acidic surfaces, but it is trivial as far as catalysis is concerned. The major catalytic sequences which are almost quantitative are those shown in schemes 1 and 2, but here it is the less stable chemisorbed carbenium ions which are involved.

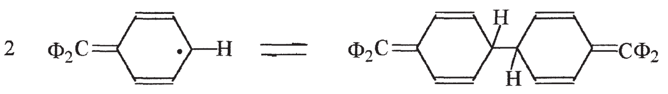
The second important point is that reaction may occur via less stable canonical forms of resonance hybrids. This has also been shown by several related examples, the most famous being that of the dimerization of the $\Phi_3C^{\cdot}$ free radical (Gomberg free radical) which is now known to occur



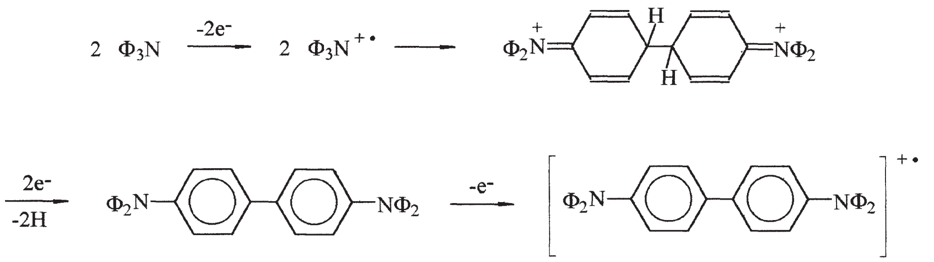
Scheme 6.



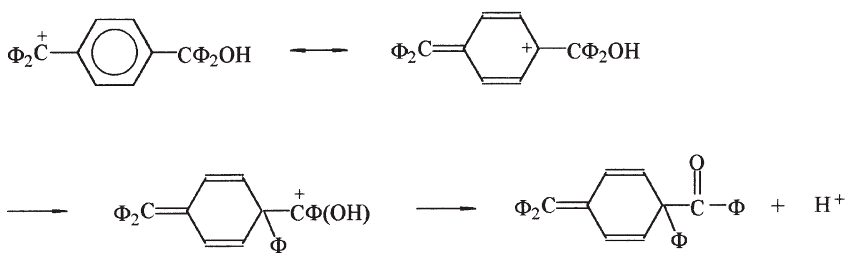
Scheme 7.



Scheme 8.



Scheme 9.



Scheme 10.

completely via the less stable canonical form, as shown in scheme 8 [10]. We have also shown that triphenylamine on silica–alumina dimerizes via the cation-radical of the monomer [11], as shown in scheme 9, and that the initial dimer loses two H atoms and then converts to a very stable cation-radical, blue-black in colour (λ_{max}, 650–700 nm).

The reaction depicted in scheme 9 using ESR analysis is a very good test for even weakly electron-deficient sites on solids. Thus ionic Pt centres on reduced Pt/MgO prepared from chloroplatinic acid and still containing traces of Cl^- ions give a positive response; PtO_2 *per se* is also active, but not when it is reduced in H_2.

A very interesting and recent example of reaction via less stable canonical forms of carbenium ions is one where there is a 1,2-intramolecular shift of an aryl group, as shown in scheme 10 [12]. Again, a methylene-1,4-cyclohexadiene central feature is of key significance.

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