Mechanism of Photolytic Formation of Trityl Ions from Triphenylmethane on Acidic Solids

By **Barry R. T. Garrett** and **John J. Rooney,*** Department of Chemistry, Queen's University, Belfast

The mechanism of the photo-generation of Ph_3C^+ ions from Ph_3CH on the surfaces of acidic solids is deduced from observations on the chemisorption of Ph_3CH, Ph_3COH, and related compounds on anhydrous magnesium perchlorate and zirconium phosphate. Protonation of one of the phenyl groups of Ph_3CH is followed by light absorption and elimination of the tertiary proton from the carbonium ion in the excited state. The net result is an endothermic isomerization to diphenylmethylenecyclohexadiene which rapidly yields the Ph_3C^+ ion by loss of a hydride ion, especially in the presence of O_2, at acidic sites.

DURING the last decade there has been considerable interest,[1-4] and controversy,[5,6] concerning the mechanism(s) of generation of Ph_3C^+ ions from Ph_3CH on acidic surfaces, the main objective being to establish whether or not silica–alumina cracking catalysts possess Lewis acidity capable of abstracting H^- ions from paraffins. The major findings were that there are two mechanisms, one of which is due to a limited number (6×10^{11} cm^{-2}) of strongly acidic protons which catalyse reactions (1) and (2) in the dark.[7] The other mechanism requires the presence of light, and if O_2 is present, the concentration of Ph_3C^+ ions approaches that (5×10^{12} cm^{-2}) obtained by direct chemisorption of Ph_3COH.[4] Since Ph_3COH was obtained when Ph_3C^+ ions formed from Ph_3CH on silica–alumina surfaces were washed off by aqueous acetone, there was considerable speculation that the photo-reaction is oxidation to Ph_3COH or Ph_3CO_2H, followed by rapid conversion to Ph_3C^+ ions at Brønsted and/or Lewis acid sites.[2,4]

$$Ph_3CH + H^+ \longrightarrow C_6H_6 + Ph_2CH^+ \quad (1)$$

$$Ph_2CH^+ + Ph_3CH \longrightarrow Ph_3C^+ + Ph_2CH_2 \quad (2)$$

RESULTS AND DISCUSSION

Anhydrous $Mg(ClO_4)_2$ (A) did not react in the light or dark with Ph_3CH or Ph_2CHOH but immediately gave the intense yellow colour of Ph_3C^+ ions when in contact with Ph_3COH. Activated $Zr(HPO_4)_2,H_2O$ (B) reacted in a similar fashion with Ph_3COH but also gave no colour with Ph_2CHOH (Ph_2CH^+ ion is also yellow). However, while Ph_3CH did not react in the dark a yellow colour slowly developed in daylight and rapidly when irradiated by a Philips 60 W bulb. By using a series of filters light in the wavelength range 370—410 nm was found to be effective.

The indicator dicinnamalacetone responds to Brønsted sites with strength $\geqslant 48$ wt % aq. H_2SO_4, the proton adduct being mauve. Addition of this indicator to (A) and (B) gave light orange and brick-red colours respectively showing that while (A) has only Lewis acidity, (B) possesses both Brønsted and Lewis acidity.[8] Moreover the results with Ph_3COH and Ph_2CHOH establish that these Brønsted sites have strengths $\geqslant 50$ but not $\geqslant 77$ wt % aq. H_2SO_4. The reaction of Ph_3COH on (A) also shows that alcohol indicators are not specific for

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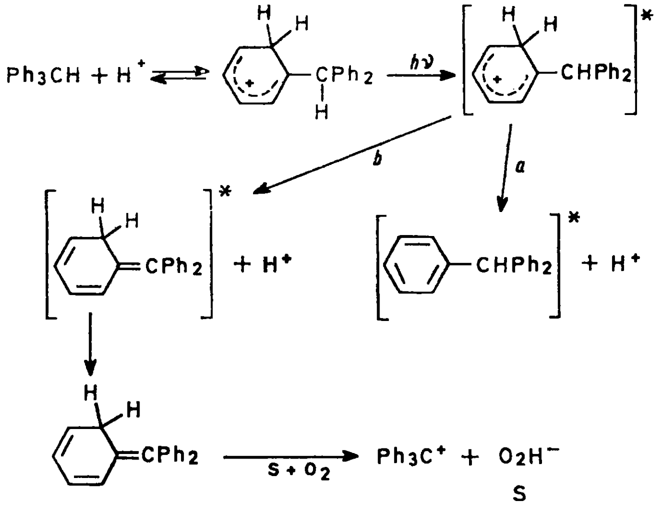
[2] A. E. Hirschler and J. E. Hudson, *J. Catalysis*, 1964, **3**, 239.
[3] H. P. Leftin and M. C. Hobson, jun., *Adv. Catalysis*, 1963, **14**, 115.
[4] R. P. Porter and W. K. Hall, *J. Catalysis*, 1966, **5**, 366.
[5] W. K. Hall and R. P. Porter, *J. Catalysis*, 1966, **5**, 544.
[6] A. E. Hirschler, *J. Catalysis*, 1966, **5**, 390.
[7] C. Yong Wu and W. K. Hall, *J. Catalysis*, 1967, **8**, 394.
[8] H. V. Drushel and A. L. Sommers, *Analyt. Chem.*, 1966, **38**, 1723.

Brønsted sites as previously argued.[1] A solution of Ph_3CH which had been irradiated while in contact with B for 24 h was filtered off and added to (A) but there was no colouration, so Ph_3COH was not generated in solution by (B).

The advantage of using (B) rather than silica–alumina is that the Brønsted sites are not strong enough to catalyse the dark reactions (1) and (2) so this complication is avoided. However protonic sites are clearly involved in the photolytic reaction as shown by the distinction in reactivities of (A) and (B) towards Ph_3CH in light. The active wavelength range reveals that the primary step is protonation of a phenyl group since O_2 does not absorb in this range but protonated benzene, toluene, and similar molecules do.[9,10]



The Scheme where S is either a protonic site or a metal cation, *e.g.* Al^{3+} in silica–alumina, explains the photolytic reaction. The net result of protonation of Ph_3CH and light absorption by the initial carbonium ion is an endothermic isomerization to the substituted methylenecyclohexadiene which should rapidly form the Ph_3C^+ ion as shown. The reactivity of the ring methylene hydrogens is evident from the previous report [11] of ready isomerization of a methylenecyclohexadiene to toluene. The final steps in conversion into Ph_3C^+ ions may involve radical intermediates since an e.s.r. analysis of a system of Ph_3CH and silica–alumina showed after irradiation for 1·5 h a small concentration of $2{\cdot}5 \times 10^{17}$ organic radicals per g of catalyst. Since reaction (*b*) has a reasonable probability of occurring, compared to reaction (*a*), only when the initial carbonium ion is in the excited state, photon absorption must cause a drastic change in the relative acidities of the different protons, methylene and tertiary, in this ion. If the phenyl group is protonated in the *para*-position during excitation an analogous scheme can be written.

EXPERIMENTAL

$Mg(ClO_4)_2$ (' Anhydrone '; Davidson and Hardy) was crushed in a dry box and particles (60—85 mesh) activated by outgassing in a vacuum line at 164° for 24 h.

$Zr(HPO_4)_2,H_2O$.—$Zr(NO_3)_4$ (50 g; Johnson Matthey) was dissolved in de-ionized water (1·5 dm^3) and AnalaR H_3PO_4 added at 90° until precipitation ceased. The solid was filtered off, thoroughly washed with hot de-ionized water, dried at 150° for 14 h, and particles (60—85 mesh) activated in air at 550° for 35 min.

Silica–alumina (25% Al_2O_3) was activated in air at 550° for 3 h. Ph_3CH, Ph_3COH, Ph_2CHOH, and dicinnamalacetone were supplied by Eastman Kodak. Ph_3CH was freed from its main impurity, Ph_3COH, by allowing a saturated solution in n-pentane to stand over several portions of activated silica–alumina. The solution was used immediately. The activated solids were placed in a desiccator and, having cooled to room temperature, were transferred in a dry box to saturated solutions of each substrate in n-pentane. The latter was purified by distillation and then by standing over activated silica–alumina for 24 h. The filters were from Kodak and were fitted into a wall of a rectangular bright aluminium box which was sealed after inserting the sample.

[4/080 *Received*, 17*th January*, 1974]

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