Catalysis of the Diels–Alder reaction by solids

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ABSTRACT

Catalysis of the Diels–Alder reaction between simple dienes and acrolein is catalysed by silica, carbon, magnesium perchlorate and the organic compound *bis*-resorcinolanthracene, all in the solid state. Quantification allows the catalysis to be identified as predominantly general acid for silica, pre-organisation of diene for carbon and *bis*-resorcinolanthracene, and Lewis acid for magnesium perchlorate. For the last, heterogeneous catalysis is far greater than homogeneous and an explanation for this is suggested.

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1. Introduction

Heterogeneous catalysis in organic chemistry covers a vast range of reactions and research is this field is ongoing and ever expanding [1–7]. Much of this involves traditional homogeneous catalysts on heterogeneous support [8–10], or catalysis by specially treated or activated heterogeneous solids [11–19], including functionalised silica-based solid acids, [14,18,20] or reactions in the presence of [21–24], or on the surface of, reactive solids [25].

Catalysis by more mundane and common solids without special activation or obvious chemical reactivity is far less common. A good example of such a solid is silica, widely used as a stationary phase in chromatography because of its ability to physi-absorb, but usually considered to be chemically inert. However, experienced organic chemists will invariably recall cases of chemical transformation following contact with this 'inert' solid [26–28], and in fact its use for chemical transformation is quite common [29].

The range of reactions amenable to heterogeneous catalysis is wide, with oxidation and reduction prominent. However, catalysis of the Diels–Alder reaction (long known in its homogeneous form) by material in the solid state has received less attention, particularly in terms of quantification [30]. The effect of added silica on the Diels–Alder reaction has been reported [31], but this was some time ago, and the underlying reason for the catalysis is still unclear.

In order to probe catalysis of the D–A reaction by solids, we have examined several common solids, and focussed on four, each displaying different (although not exclusive) catalytic properties, namely, silica as a Brønsted acid, carbon as a surface-active material, and solid magnesium perchlorate Mg(ClO$_4$)$_2$ (MPC) as a Lewis acid. In addition, catalysis by an organic solid known to effect heterogeneous catalysis of the D–A reaction, *bis*-resorcinolanthracene [32], was studied.

2. Experimental

2.1. General methods

Solvents were dried according to literature methods [33]. Chemicals were supplied by Acros Organics, Aldrich or Fisher Scientific. All starting materials obtained from an external source were checked by TLC and ^{1}H NMR where applicable prior to use.

Heterogeneous catalysis experiments were carried out on BDH Medical Supplies silica gel 60, 33–70 μm (pore size: 60 Å, surface area: approximately 500 m^2/g, oven-dried). Carbon was supplied by BDH Chemicals and magnesium perchlorate (∼250–400 μm) by Mallinckrodt Chemicals.

Gas chromatography was carried out using dodecane as an internal standard. Temperature was maintained, usually at 25 °C, by carrying out reactions in a thermostatted water-bath. Where errors in raw data are explicit (*e.g.* 52 ± 1%), the error relates to the standard deviation of at least two independent experiments.

2.2. Typical procedure: kinetics of the acrolein/1,3-cyclohexadiene reaction in the presence of a silica 'suspension'

Acrolein (1.00 g, 17.9 mmol) was added to dodecane (100 mg, 0.59 mmol). Then 450 μl of this mix comprising acrolein (340 mg, 6.07 mmol) and dodecane (34 mg, 0.20 mmol) was then added to 1,3-cyclohexadiene (2.87 ml, 2.41 g, 30 mmol). Silica (0.5, 1 and 1.5 g, 0.0083, 0.017 and 0.025 mol, respectively) was then sprinkled into 3 ml of the reaction mix (acrolein 5.48 mmol, dodecane

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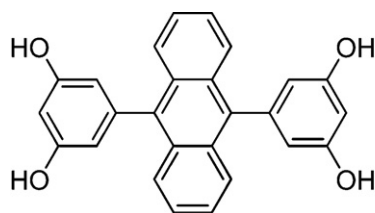
*bis*resorcinolanthracene
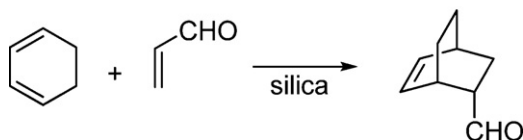
Scheme 1. D–A reaction of acrolein with 1,3-cyclohexadiene.

0.18 mmol and 1,3-cyclohexadiene, 27.11 mmol) and the supernatant liquid monitored by GC at various time intervals.

3. Results and discussion

3.1. Preliminary selection of catalysts

A range of solids was screened for catalysis of the D–A reaction by allowing a 1:5 molar ratio mixture of acrolein and 1,3-cyclohexadiene to impregnate the solid (typically between 3:1 and 191:1 molar ratio of solid to acrolein). After 24 h only carbon (ninefold), aluminium chloride (sixfold), MPC (27-fold) and silica (10-fold) showed any enhancement of conversion to cycloadduct relative to the control (5% after 24 h at rt). For aluminium chloride precise kinetic data proved to be difficult to obtain and this was not investigated further.

3.2. Catalysis by silica

The reaction of acrolein and 1,3-cyclohexadiene in the presence of a suspension of silica was monitored; silica gel 60, 30–70 μm, pore size 60 Å, surface area 500 m^2 g^{-1} was used, and the molar ratio of acrolein–cyclohexadiene–silica was 1:5:3. The amount of adduct, *endo*-bicyclo[2,2,2]oct-5-ene-2-carbaldehyde (Scheme 1), was determined by GC (using dodecane as internal reference) and plotted against time (Fig. 1).
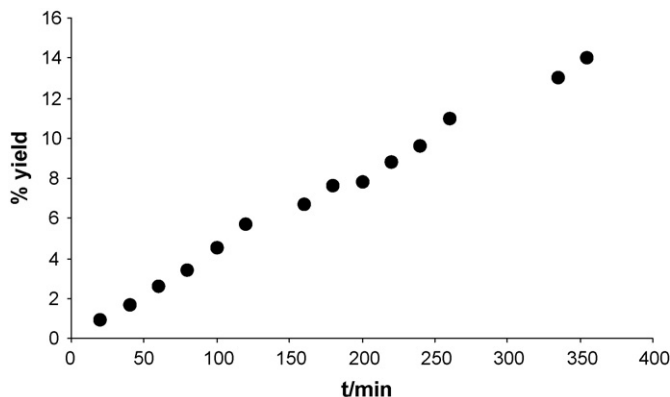
The data of Fig. 1 were analysed using the 'initial rates' method [34], using the data from the first 5% of conversion to give $V_i = d$[cycloadduct]/$dt = -d$[acrolein]/$dt = 8.58 \times 10^{-4}$ M^{-1} min^{-1}. A duplicate run gave $V_i = 10.87 \times 10^{-4}$ M^{-1} min^{-1}, a mean of $(9.7 \pm 1.1) \times 10^{-4}$ M^{-1} min^{-1}. The reaction was repeated in the presence of different amounts of silica to give the data of Table 1. There is an approximately linear dependence on the amount (nominal concentration) of suspended silica (Fig. 2).

Comparing the values of V_i in the presence of silica with that for the control, a quantitative assessment of the rate-enhancement can be shown as V_i(catalysed) = V_i(control) + a['silica'] where a is 1.33×10^{-4} min^{-1}, ['silica'] is the nominal amount of silica added in moles per dm^3 of reaction solution, and V_i(control) is the initial rate in the absence of suspended silica (see entry 1 of Table 1). For comparison of different reactions, under the same conditions of concentration, *etc.* and in the presence of the catalyst, the enhancement relative to the control is important, here defined as a/V_i(control); in this case a/V_i(control) = 2.6 M^{-1}.

Silica is an acidic material because of Brønsted acid sites, estimated at 1500 μmol/g [35], and this equates to 0.09 mol acid 'sites' per mol silica. So the V_i(catalysed) equation above can be re-written as V_i(catalysed) = V_i(control) + b['silica Brønsted sites'] where b is 1.48×10^{-3} min^{-1}; b/V_i(control) = 28 M^{-1}.

General acid catalysis of the D–A reaction was studied by Wassermann in the 1930s and 1940s [36,37]. Homogeneous catalysis of the benzoquinone–cyclopentadiene reaction by 1 M chloroacetic acid (pK_a 2.87 [38]) in benzene gave a 20-fold rate enhancement. For the reaction in the present case using heterogeneous silica (albeit that between acrolein and cyclohexadiene) the enhancement is similar as reflected in the b/V_i(control) term of 28 M^{-1}. Since the SiOH group has an effective p$K_a \geq 4$ [20], this suggests that D–A catalysis by heterogeneous acid is comparable to, or even surpasses, that by homogeneous acid.

Experiments where the reaction mix was allowed to impregnate the solid can also be analysed to give a value for a. The molar ratio under these conditions was acrolein–cyclohexadiene–silica 1:5:37. The yield after 24 h was 41% compared with <5% for control; this

Fig. 1. Plot of % yield of adduct *vs.* time for reaction of 1:5 mole–mole acrolein–1,3-cyclohexadiene (3 ml) in the presence of silica (1 g), T = 25 °C.
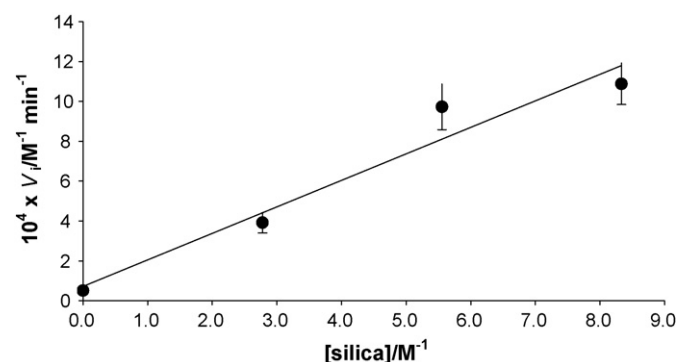

Fig. 2. Plot of initial rate (V_i) data for the reaction of acrolein with 1,3-cyclohexadiene *vs.* added silica. Reaction volume 3 cm^3, T = 25 °C.
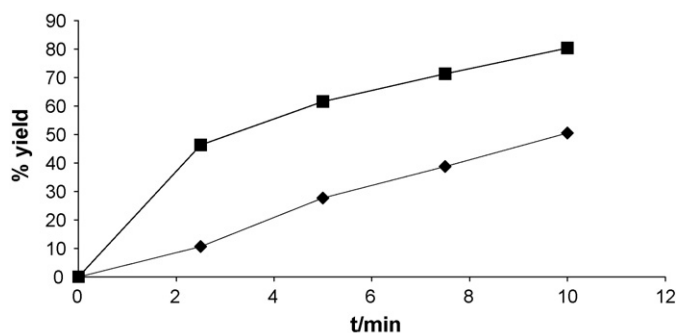
Fig. 3. Plot of % yield of adduct *vs.* time for reaction of 1:5 mole–mole acrolein/1,3-cyclopentadiene (12 μl) impregnated into silica (50 mg) (■ = impregnated reactions, ♦ = control.

eightfold enhancement can be used to calculate an approximate value for $a = 0.053 \times 10^{-4}$ min^{-1} and $b = 0.59 \times 10^{-4}$ min^{-1}; values for a/V_i(control) and b/V_i(control) are 0.10 and 1.13 M^{-1}, respectively. This apparently lower enhancement is because much if the solid silica is 'unused' as the amount of solution is insufficient to saturate the solid.

The reaction between acrolein and 1,3-cyclopentadiene was also investigated under the same 'impregnated' silica conditions, a 1:5:33 ratio of acrolein–diene–silica, and gave the plot in Fig. 3. It is clear that there is some catalysis of the reaction by silica, particularly in the early stages, with rate enhancement of ~fourfold allowing an approximate calculation of $a = 66 \times 10^{-4}$ min^{-1} and $b = 729 \times 10^{-4}$ min^{-1}. The values for a/V_i(control) and b/V_i(control) are 0.044 and 0.48 M^{-1}, respectively; again this lower enhancement is because the amount of solution is insufficient to saturate the solid. It is noteworthy that the enhancements for both the cyclohexadiene and cyclopentadiene reactions with acrolein when impregnated onto silica are of the same order of magnitude, reinforcing the proposal that silica catalysis is effectively by Brønsted acid acting on the acrolein.

3.3. Catalysis by carbon

A similar analysis of reactivity for a 1:4.5 mix of acrolein–cyclohexadiene in the presence of suspended carbon gave an enhancement V_i(catalysed) = V_i(control) + a['carbon'] where a is 0.15×10^{-4} min^{-1}. The value of a/V_i(control) is 0.27 M^{-1}. Similar experiments were carried out using acrolein and isoprene (2-methylbuta-1,3-diene), acrolein and cyclopentadiene, and methyl acrylate and cyclopentadiene; the enhancement data are summarised in Table 2.

Compared with cyclohexadiene and isoprene, there is clearly no enhancement for cyclopentadiene. For the acrolein dienophile it might be argued that this is related to the fact that the un-catalysed reaction is very fast anyway, but the intrinsically slower methyl acrylate reaction is not accelerated either. Carbon is known to have

Table 2
Reactivity enhancement data for the reactions of acrolein and methyl acrylate with 1,3-cyclohexadiene, isoprene or cyclopentadiene in the presence of carbon.

Dienophile	Diene	a (min^{-1})	a/V_i (control) (M^{-1})
Acrolein	Cyclohexadiene	0.15×10^{-4}[a]	0.27[b]
Acrolein	Isoprene	1.02×10^{-4}[a]	0.13[b]
Acrolein	Cyclopentadiene	0	0.00
Methyl acrylate	Cyclopentadiene	0	0.00

Reaction volume 2.7–3 cm^3, $T = 25\,^\circ$C.

[a] The value of b ('a' re-defined in terms of 'acid sites') is 35.7×10^{-4} min^{-1} for cyclohexadiene and 243×10^{-4} min^{-1} for isoprene.

[b] The values of b/V_i(control) are 64 M^{-1} for cyclohexadiene and 31 M^{-1} for isoprene.

potential Brønsted acid sites, but general acid activation of acrolein would give similar enhancement irrespective of the diene. Adsorption of the reagents onto the surface thereby increasing the effective concentration is also unlikely; firstly because the control reaction is essentially a neat (solvent-free) concentrated mixture of reagents anyway, and secondly because it is difficult to see why cyclopentadiene would behave differently. The simple carbon used here exhibits a broad range of porosity, with pore sizes from a few nm upwards. Pores at the lower end of this range would be a 'tight fit' for the molecules here, and we believe that the effect is to force the diene towards a more TS-like conformation; this would explain the minimal effect for the already optimised cyclopentadiene. As with silica, a reduced enhancement was seen for the 'impregnated' case.

3.4. Catalysis by magnesium perchlorate

Catalysis of the D–A reaction by added magnesium perchlorate (MPC) is well-known. However, studies are generally on cases of homogeneous catalysis [39], although catalysis of a 1,3-dipolar cycloaddition involving a solid-supported chiral ligand in solutions containing MPC has been reported [40]. In most cases, the soluble salt provides Mg^{2+} ions to act as a Lewis acid, and the solvent used is CH$_2$Cl$_2$ or MeCN.

We noted the insolubility of MPC in 1,3-cyclohexadiene and decided to use the acrolein–cyclohexadiene reaction to explore the potential for *heterogeneous* D–A catalysis. Results for the reaction of acrolein–1,3-cyclohexadiene in the presence of suspended MPC (the molar ratio of acrolein–cyclohexadiene–MPC was 1:5:0.16) are plotted in Fig. 4. The sigmoidal plot at first suggested to us slow dissolution of MPC and catalysis by *homogeneous* Lewis acid. However, no obvious dissolution of the solid was visible, and samples of the supernatant liquid, removed at 60, 135, and 155 min (the start, middle and end, respectively, of the rapid rate increase) showed subsequent reaction rate little different to the control. It is clear, therefore, that catalysis is *heterogeneous*. Concentrating on the latter part of Fig. 4 (after 100 min), where catalysis appears to be greatest, a pseudo first-order rate constant of $k_{obs} = 0.039$ min^{-1} was calculated. Translating this to conditions used for initial rate analysis of the silica and carbon catalyses gives $a = 2378 \times 10^{-4}$ min^{-1} and a/V_i(control) = 4573 M^{-1}.

So, it is clear that catalysis *is* by heterogeneous MPC, and that it is significant. Direct comparison with the homogeneous case is not possible because MPC is very insoluble in the reaction mix. However, it is more soluble in an acrolein-rich 1:1 dienophile-diene mix, and reaction under these conditions showed a 10-fold rate enhancement over control for a 0.098 M solution of MPC. This translates to a value for $a = 100 \times 10^{-4}$ min^{-1} and for a/V_i(control) = 92 M^{-1}.
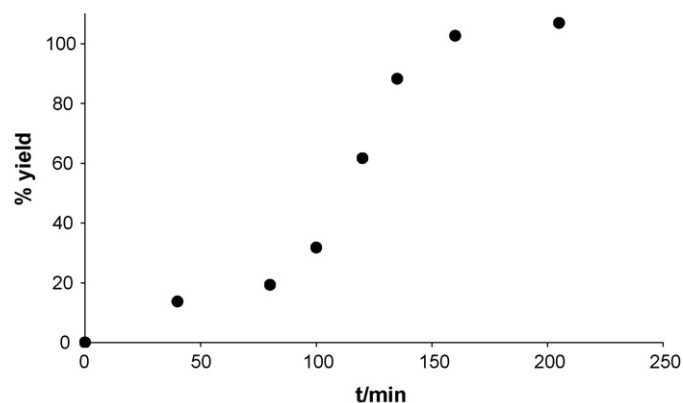

Fig. 4. Plot of % yield of adduct *vs.* time for reaction of 1:5 mole–mole acrolein–1,3-cyclohexadiene (3 ml) in the presence of MPC (200 mg), $T = 25\,^\circ$C.
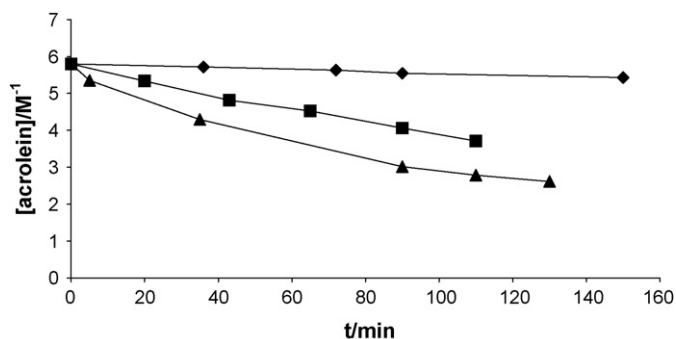
Fig. 5. Plot of [acrolein] *vs.* time for homogeneous reaction of 1:1 mole–mole acrolein–isoprene with dissolved MPC ($\blacklozenge$ = 0.096 M, $\blacksquare$ = 0.193 M, $\blacktriangle$ = 0.288 M), T = 25 °C.

Clearly, heterogeneous catalysis by MPC is significantly more efficient than homogeneous.

In contrast to the cyclohexadiene case, MPC was found to be quite soluble in isoprene and so homogeneous catalysis of a 1:1 mole–mole acrolein–isoprene mix by this catalyst was also studied and gave the results shown in Fig. 5. The plots were analysed assuming a first-order dependence on [acrolein] as $-d[\text{acrolein}]/dt = k_{obs}[\text{acrolein}]$, where $k_{obs} = k\,[\text{MPC}]_0$. The term k is calculated from the data of Table 3 and is the bimolecular constant for reaction of the *complexed* acrolein with isoprene. The value of the bimolecular constant for the uncatalysed reaction (although measured for the 1:5 mix) is approximately $6.52 \times 10^{-6}\,\text{M}^{-1}\,\text{min}^{-1}$ so the complexation in solution increases the rate by at least 3512-fold. For comparison with the earlier reactions analysed by the initial rate method, where $V_i(\text{catalysed}) = V_i(\text{control}) + a[\text{catalyst}]$, the term a can be shown to be given by $k[\text{diene}]_0$, which is 0.131 min^{-1}; the term $a/V_i(\text{control})$ is 604 M^{-1}. Although for a different diene, this homogeneous enhancement is well below the value (4573) for the heterogeneous reaction.

We speculate on a possible reason for the extreme enhancement of the Diels–Alder reaction by heterogeneous MPC, even in comparison with homogeneous MPC. To begin with, despite the MPC being nominally 'anhydrous', it is an extremely hygroscopic material and it can be assumed that the surface layer is more akin to hydrated MPC, $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. Based on NMR studies it has been proposed that the $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystal structure resembles that of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$,[41] which has the metal ion coordinated by a regular octahedron of water molecules. Computational modelling of the solid state structure of MPC is beyond the scope of this work, but we have modelled (at B3LYP/6-31G*) the $\text{Mg}^{2+}(\text{H}_2\text{O})_6$ and replaced each water successively with acrolein from $\text{Mg}^{2+}(\text{H}_2\text{O})_5(\text{C}_3\text{H}_4\text{O})$ through to $\text{Mg}^{2+}(\text{C}_3\text{H}_4\text{O})_6$. The $\text{Mg}^{2+}(\text{H}_2\text{O})_5(\text{C}_3\text{H}_4\text{O})$ might approximate to the situation of an acrolein bound to the heterogeneous surface, and the $\text{Mg}^{2+}(\text{C}_3\text{H}_4\text{O})_6$ to the situation in acrolein-rich homogeneous solution. The B3LYP/6-31G* calculated energies for the acrolein-centred LUMO (*i.e.* that of the dienophile) increase as acrolein replaces water, so that the LUMO energy is lowest for a

Table 3
First-order rate constants k_{obs} and second order constant k for reaction of 1:1 mole–mole acrolein–isoprene with dissolved MPC.

MPC (M)	k_{obs} (min^{-1})	k [b] (M^{-1} min^{-1})
0[a]	0.37×10^{-4} [a]	
0.096	4.45×10^{-4}	
0.193	3.89×10^{-3}	0.0229
0.288	5.86×10^{-3}	

At t = 0, acrolein = 5.80 M; isoprene = 5.74 M, dodecane = 0.19 M. T = 25 °C.
   [a] Estimated based on value of k_2 for 1:5 mole–mole reaction.
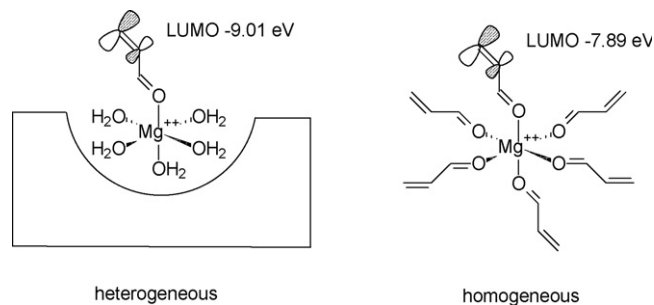   [b] Slope of plot of k_{obs} *vs.* MPC.

Fig. 6. LUMO energies (B3LYP/6-31G*) of acrolein complexed to solid MPC and dissolved MPC.
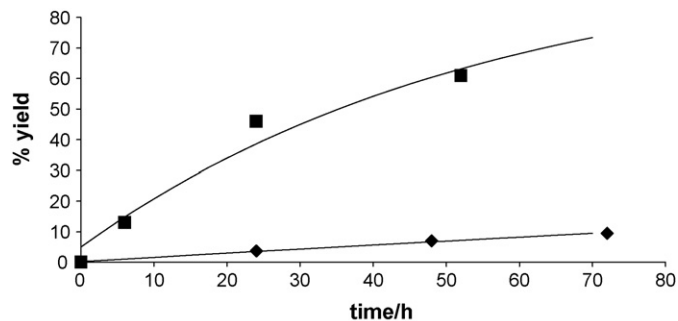

Fig. 7. Plot of % yield of adduct *vs.* time for reaction of 1:5 mole–mole acrolein–cyclohexadiene (217 μl) with suspended *bis*-resorcinolanthracene ($\blacklozenge$ [bRA] = 0 mg, $\blacksquare$ [bRA] = 5 mg, 12.7 μmol, 0.058 M (nominal)).

single coordinated acrolein. In effect, dienophile coordinated to Mg 'buttressed' by the interior waters of the solid is more reactive than that coordinated to Mg in solution (Fig. 6).

3.5. Catalysis by organic solid

The time course of the reaction of 1:5 mole–mole acrolein–cyclohexadiene with suspended *bis*-resorcinolanthracene (bRA) is shown in Fig. 7. Kinetic analysis gives an approximate value for the parameter $a = 8.43 \times 10^{-3}$ min^{-1} $a/V_i(\text{control}) = 163$ M^{-1}. These results are similar to those found by Endo et al. [32].

A similar reaction was carried out using 1:5 acrolein and cyclopentadiene and the time course is shown in Fig. 8. The value for the parameter a is 2.20 min^{-1} and $a/V_i(\text{control}) = 7$ M^{-1} for the acrolein–cyclopentadiene reaction. The % *exo* at 25% was only marginally different from control at 22%. Similarly the data for the reaction of acrolein with isoprene is shown in Fig. 9 and the parameter $a = 2.72 \times 10^{-3}$ min^{-1} and $a/V_i(\text{control}) = 29$ M^{-1}. Experiments were also carried out with methyl acrylate and cyclopentadiene,
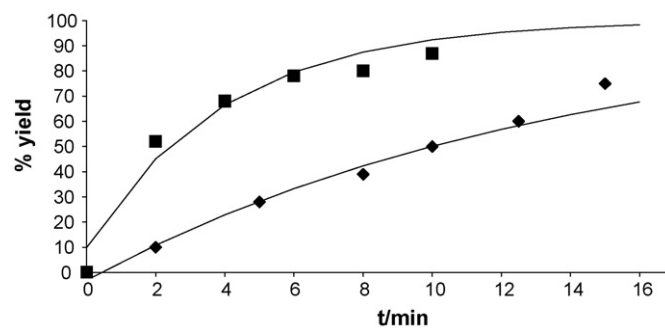

Fig. 8. Plot of % yield of adduct *vs.* time for reaction of 1:5 mole–mole acrolein–cyclopentadiene (324 μl) with suspended *bis*-resorcinolanthracene ($\blacklozenge$ [bRA] = 0 mg, $\blacksquare$ [bRA] = 5 mg, 12.7 μmol, 0.039 M (nominal)).
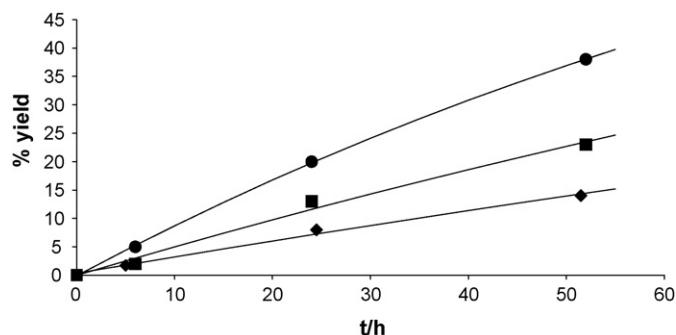
Fig. 9. Plot of % yield of adduct *vs.* time for reaction of 1:5 mole–mole acrolein–isoprene (369 μl) with suspended *bis*-resorcinolanthracene (♦ [*b*RA] = 0 mg, ■ [*b*RA] = 5 mg, 12.7 μmol, 0.034 M, ● [*b*RA] = 10 mg, 25.4 μmol, 0.069 M (concs. nominal)).

Table 4
Rate enhancements for Diels–Alder reactions in the presence of suspended *bis*-resorcinolanthracene.

	a (10^4 min^{-1})	a/V_i (control) (M^{-1})
Acrolein–cyclohexadiene	84.3[a]	163[a]
Acrolein–cyclopentadiene	22,000	7
Acrolein–isoprene	27.2	29
Methyl acrylate–cyclohexadiene	5[b]	98[b]
Methyl acrylate–cyclopentadiene	0	0

T = 25 °C.

[a] Using the data of Endo et al. [32], the term a = 33–55 × 10^{-4} min^{-1} and a/V_i(control) = 92–153 M^{-1}.

[b] Using the data of Endo et al. [32].

but no significant acceleration was observed. The results for catalysis by *b*RA are summarised in Table 4, which includes some relevant literature data [32].

For the acrolein–cyclohexadiene reaction, Endo et al. have presented good evidence for heterogeneous, rather than homogeneous catalysis by *b*RA [32]. They proposed that reaction occurs catalytically in the cavities of the solid *b*RA, and that following assembly of the two reactants in the cavity, a preorganised reaction occurs with high rate enhancement. We can support this for reactions involving cyclohexadiene, but suggest that the cavities favour preorganisation towards the TS involving *cyclohexadiene only*. The enhancements, reflected in the a/V_i(control) term, for the same dienophile, but different dienes (cyclopentadiene and isoprene) are significantly lower. Endo et al. also noted the enhancements for homogeneous general acid catalysis of the acrolein–cyclohexadiene reaction by dissolved *b*RA and by dissolved resorcinol; these can be re-defined in terms of a and a/V_i(control) as (dissolved *b*RA) a = 3.33 × 10^{-4} min^{-1} and a/V_i(control) = 9.3 M^{-1}, and (dissolved resorcinol) a = 4.50 × 10^{-4} min^{-1} and a/V_i(control) = 12.6 M^{-1}, respectively. The enhancements a/V_i(control) for our heterogeneous reactions involving isoprene and cyclopentadiene are of this magnitude, suggesting that heterogeneous catalysis for reactions involving these dienes is probably due mainly to a general acid affect (on the dienophile), rather than the diene pre-organisation effect seen for cyclohexadiene.

4. Conclusions

We confirm the existence of different types of heterogeneous catalysis of the Diels–Alder reaction by solids, but have identified some intriguing extra factors. Catalysis by solid silica is predomi-

nantly a general acid type; likewise with *b*RA for cyclopentadiene and isoprene. For carbon and the *b*RA with cyclohexadiene, catalysis for cyclohexadiene is predominantly due to pre-organisation of the diene towards a TS-like structure in the pores and cavities of the solid. Most intriguing is catalysis by solid magnesium perchlorate; this is almost certainly of the Lewis acid type, but the remarkable enhancement by the solid is worthy of further investigation.

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