A concerted mechanism for uncatalysed transfer of carbon substituents from diimides to C=C and C≡C

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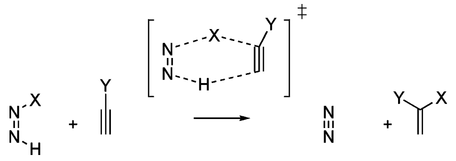
We present high-level computational predictions regarding a novel uncatalysed, yet feasible, C–C bond forming reaction.

The reduction of alkenes or alkynes with *cis*-diimide is a remarkable reaction in the sense that hydrogen is transferred to a carbon–carbon multiple bond without the need for any catalyst.[1] Solvent effects are virtually absent, and a large variety of oxidation agents can be used for the generation of *cis*-diimide by oxidation of hydrazine.[1] The reaction proceeds through a six-membered concerted transition state,[2,3] and in the present communication, we want to address the question of whether this reaction can be generalised to include alkyl- or aryl-substituted diimides, which would constitute a new type of a formally non-catalysed addition of R–H or Ar–H to an alkene or alkyne. Hydroformylation, which is the formal addition of H–CH=O to a double bond, requires metal-catalysis, and is a reaction of tremendous industrial importance.[4,5] The feasibility of such an uncatalysed reaction is addressed by high-level computational predictions on a potential candidate for a totally novel uncatalysed C–C forming reaction, namely the concerted transfer of a carbon substituent from a substituted diimide to a C=C or C≡C bond (Scheme 1).



Scheme 1

Table 1 Barriers and reaction energies for transfer HN=NX + ethylene → N_2 + CH_3CH_2X[a]

X	Barrier	Reaction energy
H	10.7	−352.8
CH_3	183.3	−346.0
$H_2C{=}CH$	169.9	−335.1
Ph	155.3	−344.9
p-NO_2-Ph	145.7	−353.9
$CONH_2$	133.9	−325.8
COOMe	103.2	−340.8
HC≡C	120.3	−383.0
CHO	92.4	−345.2
CN	79.9	−411.0

[a] G3(MP2)//B3LYP values in kJ mol^{-1} at 0 K.

Table 2 Barriers and reaction energies for transfer HN=NX + acetylene → N_2 + CH_2CHX[a]

X	Barrier	Reaction energy
H	15.7	−395.4
CH_3	188.1	−399.2
$H_2C{=}CH$	169.8	−401.7
Ph	155.4	−403.2
p-NO_2-Ph	145.3	−410.3
$CONH_2$	141.2	−370.9
HC≡C	114.3	−437.9
COOMe	103.1	−384.2
CHO	95.3	−391.4
CN	83.2	−456.9

[a] G3(MP2)//B3LYP values in kJ mol^{-1} at 0 K.

Table 3 Barriers and reaction energies for transfer HN=NX + Z → N_2 + HXZ[a]

X,Z[b]	Barrier	Reaction energy
H, $HC{\equiv}COCH_3$	19.2	−429.7
a-HC≡C, $HC{\equiv}COCH_3$	116.6	−480.9
s-HC≡C, $HC{\equiv}COCH_3$	93.5	−469.7
a-HC≡C, HC≡CF	123.0	−504.0
s-HC≡C, HC≡CF	87.8	−502.7
a-CN, HCN	77.8	−275.3
s-CN, HCN	153.2	−277.6
a-Ph, HC≡CPh	153.3	−403.0

[a] G3(MP2)//B3LYP values in kJ mol^{-1} at 0 K. [b] X and the substituent/heteroatom point in the same direction (*s*) or in opposite directions (*a*).

With the G3(MP2)//B3LYP method,[6] we have calculated a total of 28 reaction barriers and reaction energies. All calculations have been carried out with the Gaussian suite of programs.[7] The X and Y substituents have been varied to investigate the electronic requirements for the reaction at hand. The results are shown in Tables 1–3. For each of the entries in Tables 1–3 we have calculated the geometries of the reactants, the transition state (one imaginary frequency) and the products at the B3LYP/6-31G(d) level to subsequently compose the G3(MP2)//B3LYP energies that have been shown to be accurate to within 1.25 kcal mol^{-1}.[4] Examples of typical transition states for transfer to ethylene and acetylene, respectively, are shown in Fig. 1. All of the transition states that we have located are similar in appearance. They differ in the degree by which X is transferred from the diimide to the unsaturated bond. For the reactions with relatively low barriers, *e.g.* X = CHO, the N–X bond of the transition state is shorter (1.523 Å) compared to the situations where the barrier is high, *e.g.* X = CH_3

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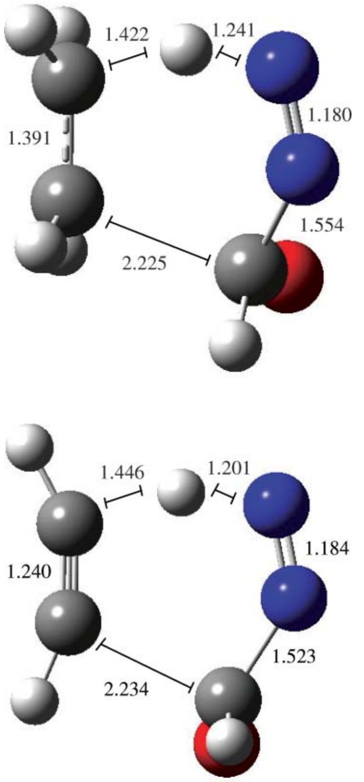

Fig. 1 Calculated transition states for the transfer of CHO to ethylene (above) and acetylene (below). Bond lengths are given in Å.

(N–X = 1.910 Å). The reason for the higher degree of transfer in the cases where the barrier is high is to be found in the fact that the reactions are highly exothermic. When a late transition state is involved, there is some lending of stability from the products. The high exothermicity of the reactions is simply reflecting the large strength of the N≡N bond; in fact, when Y = H, the spread on the reaction energies is 10% at the most. This spread increases once X and Y are varied together. However, in either case, the reaction energy does not have a large impact on the barrier—a low barrier and a large exothermicity do not go hand in hand. The reactions are more exothermic in the cases of transfer to acetylene (by 51 kJ mol^{-1} on average), which is not a surprise given the larger bond strength of the triple bond compared to the double bond.

The change in the reaction barriers as the electronic nature of X and Y are varied provides information on the fundamental electronic requirements of the reaction. The barriers for transfer to acetylene and ethylene lie within 7 kJ mol^{-1} (2 kJ mol^{-1} on average) with the transfer to acetylene being the least favourable. The reason for this is that the transition state energy is determined by the structural deformation in the transition state; this is larger in the case of acetylene as can be seen in Fig. 1.

In Tables 1 and 2 the electronic nature of the diimide substituent is varied. It is evident that the reaction is favoured by increasing electropositive character on the substituent under transfer. There is a clear correlation with the classical Hammett σ values: $\sigma(\mathrm{CH_3}) = -0.17$, $\sigma(\mathrm{Ph}) = 0.05$, $\sigma(\mathrm{COOMe}) = 0.45$, $\sigma(\mathrm{CHO}) = 0.47$, $\sigma(\mathrm{CN}) = 0.62$—the barriers decrease from CH_3 to CN. In the cases of CN and CHO, the barriers (79.9 kJ mol^{-1} and 92.4 kJ mol^{-1}, respectively) seem to be within reach of ambient reaction conditions in an organic laboratory. The availability of substituted diimides has been reported, one example is PhN=NH,[8] so the diimides associated with the lowest barriers should be experimentally accessible and from suitable precursors. The highest barrier was found for methyl transfer and probably becomes prohibitively large with a value of 183 kJ mol^{-1}. For the highest and the lowest barriers we also calculated the influence of raising the temperature to 298.15 K and it was found that the barrier was negligibly lower by 1 kJ mol^{-1}.

Given the result that the group under transfer acts as an electrophile, it would be sensible to expect that an increase in the nucleophilicity of the accepting carbon in the unsaturated moiety would decrease the barrier. This was tested in calculations of the reaction barriers for selected substituted unsaturated species to investigate inductive and resonance effects. In the case of methoxy substituted acetylene, the barrier for H-transfer increases. This is consistent with the large electronegativity of oxygen. The calculated transition state geometry shows that the hydrogen is most progressed to the opposite end of the methoxy substituent because of the resonance donation of the lone pair to that site. When the substituent under transfer is C≡CH the result seems at first to contradict that of H-transfer because the barrier is lower when C≡CH and CH_3O point in the same direction (*s* for *syn*), *i.e.*, when the donor carbon atom is electron deprived by the neighbouring oxygen atom. However, the reason for this is clearly revealed by a calculation with the NBO methodology by Weinhold *et al*.[9] The calculation shows a significant delocalisation of the oxygen lone pair of the CH_3O–C≡CH moiety into the π^* orbital of the opposite C≡CH moiety under transfer. The same effect is evident when the heteroatom is fluorine and the barriers are comparable for the *syn* as well as for the *anti* transition states. When the transfer takes place to HCN, the lowest barrier (and the lowest barrier of this study) is found for transfer to the nitrogen lone pair, *i.e.*, consistently to the most electron rich site of the molecule. An attempt was also made to bring down the barrier by insuring delocalisation all over the transition state by transfer of a phenyl group to β-styrene. This substitution pattern, however, did not reveal an effect.

Thus, in summary, it would seem that the reaction is a slightly asynchronous concerted process with the entity that is transferred from the diimide acting as the acceptor and the unsaturated carbon bond acting as the donor. The barriers of the reactions that accommodate the electronic requirements seem to be low enough for the process to provide a valuable and novel synthetic tool for uncatalysed C–C bond formation.

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