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Low-temperature reactions: Tunnelling in space

Chemical reactions with activation barriers generally slow to a halt in the extreme cold of dense interstellar clouds. Low-temperature experiments on the reaction of OH with methanol have now shown that below 200 K there is a major acceleration in the rate that can only be explained by enhanced quantum mechanical tunnelling through the barrier.

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? qtrochemists are especially interested in the detection, origin and fate of molecules in space. The clouds of gas and dust where most interstellar molecules have been found have typical temperatures of only a few degrees above absolute zero[1], so they might seem unlikely candidates to host complex chemistry; however, an extraordinarily rich variety of molecules have been detected[2]. Under such extremely cold conditions, only reactions that can roll, unhindered by barriers, down the potential energy surface that controls their behaviour have been taken into account in astrochemical models. Now, writing in *Nature Chemistry*, Heard and colleagues describe[3] the observation of a reaction that does have a significant barrier on its reaction path, yet occurs very rapidly at low temperatures by not going over the barrier but rather by tunnelling right through it.

Three general cases for exothermic reactions can be identified, as shown schematically in Fig. 1. Part a represents a reaction with a substantial barrier caused by the necessity to break chemical bonds. The upper panel depicts the potential energy (the stored internal energy) of the system as the reaction takes place, and the lower panel shows how an Arrhenius plot for such a reaction might look. The reaction slows rapidly as the temperature drops (towards the right of the plot). Although roughly linear, a slight curvature is expected and is often more evident at lower temperatures. The curvature arises in part because the pre-exponential A factor is actually slightly temperature dependent, and also because quantum mechanical tunnelling enables the system to cross to reactants at energies below the summit of the barrier.

If the two reacting species are radicals, for example CN and O_2, then there may be no barrier on the potential energy curve, as shown in Fig. 1b. The potential curve falls into a deep well as the unpaired electrons on each radical combine to form a chemical bond. In this case the reaction often becomes faster as the temperature drops, as depicted in the lower panel of Fig. 1b. Studying gas-phase reactions at temperatures much below about 200 K becomes very difficult owing to condensation on the cold walls of the reactor, but the CRESU (*cinétique de réaction en ecoulement supersonique uniforme*, which means reaction kinetics

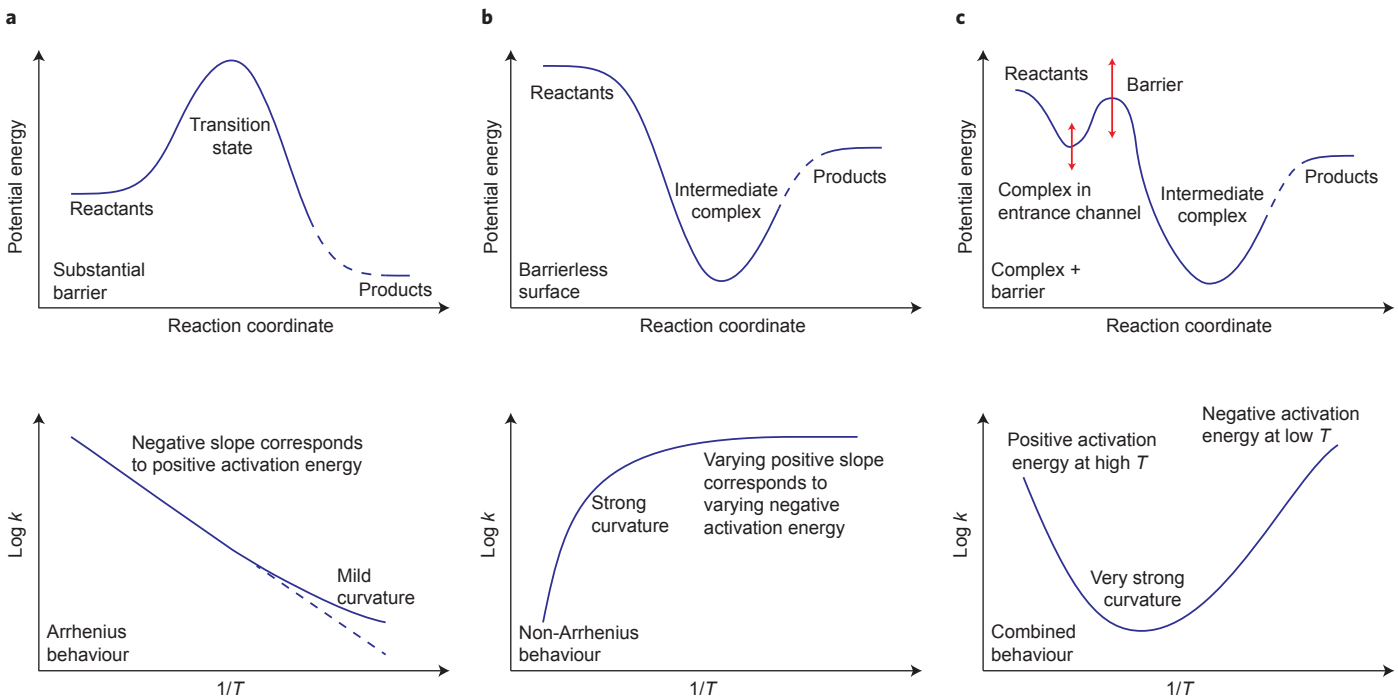

Figure 1 | General cases for exothermic reactions. To a good approximation, most chemical reactions adhere to the kinetics described by the Arrhenius equation, $k(T) = A\exp(-E_{act}/RT)$ where the temperature dependence of the rate constant is represented by a constant factor A multiplied by an exponential function. This function approximately represents the fraction of collisions at a given temperature T with enough energy to surmount the barrier, the magnitude of which is closely related to the activation energy E_{act}. A plot of the log of the rate constant as a function of inverse temperature should therefore be linear with a slope equal to $-E_{act}/R$, and is known as an Arrhenius plot. In this figure, the upper panels depict schematically the potential energy of the system as the reaction takes place, and the lower panels show how an Arrhenius plot might look for that system. **a**, A reaction with a substantial barrier, which adheres approximately to the Arrhenius equation. **b**, A reaction with no barrier, showing strongly non-Arrhenius behaviour. **c**, A reaction passing through an initial weakly bound complex and then over a barrier (which may or may not be above the reagent energy): the reaction adheres to the Arrhenius equation only at higher temperatures.

in uniform supersonic flow) technique[4] solves this by creating a wall-less flow of supercold gas by expansion through nozzles resembling rocket motor exhausts. Using this method, many reactions have been found to be barrierless, with characteristics resembling those depicted in the lower panel of Fig. 1b[5].

One of the earliest reactions to be studied at very low temperatures by the CRESU technique, $CN + C_2H_6 \rightarrow HCN + C_2H_5$, showed[6] a behaviour that is in some ways a combination of the two 'extremes' represented by Fig. 1a,b. At high temperatures it displays a positive activation energy, but as the temperature falls the rate constant passes through a minimum and then increases by almost an order of magnitude between 200 K and 23 K. This behaviour is characteristic of a system that forms an initial, relatively weakly bound complex, which then goes on to cross a barely submerged potential barrier to proceed to products (Fig. 1c). The relationship between the formation and redissociation of the initial complex versus subsequent crossing of the barrier has been invoked to explain the observed behaviour[7,8]. Further experimental and theoretical studies have shown that many radical–molecule reactions fall into this same category, but the minimum in the rate constant is not always observed in the temperature range of existing measurements because it depends strongly on the interplay between the initial well depth and subsequent barrier height, as represented by the red arrows in the upper panel of Fig. 1c.

Heard and colleagues chose to study the reaction between the hydroxyl radical and methanol at low temperatures, which can occur through two possible channels:

$$OH + CH_3OH \begin{array}{l} \nearrow CH_2OH + H_2O \\ \searrow CH_3O + H_2O \end{array}$$

Both have substantial barriers to reaction, and based on this have not been included in models of cold, dark interstellar clouds. Measurements of the overall reaction rate constant at temperatures above 200 K showed classic Arrhenius behaviour as illustrated in Fig. 1a. However, Heard and co-workers saw a dramatic upturn in the overall rate constant (as measured by the disappearance of OH) when the temperature was reduced to 63 K where the rate constant is almost two orders of magnitude greater than at 200 K.

Heard and co-workers' experiments led them to explain this behaviour through the occurrence of quantum-mechanical tunnelling, whereby light particles (such as H atoms) have a substantial probability of penetrating beneath potential energy barriers. It is well known that tunnelling results in curved Arrhenius plots, with the rate constant at low temperatures showing a tendency to level off and not descend as would be predicted by extrapolation from higher temperatures (Fig. 1a). But an enhancement of two orders of magnitude is unexpected.

Experiments that directly detected CH_3O proved that the reaction was occurring through the channel shown in Fig. 1b, but the large barrier height for this reaction (corresponding to an average collision energy at a temperature of around 1,200 K) suggested that tunnelling must play a role. Heard and colleagues suggest that, at low temperatures, the reactants form a weakly bound complex OH···CH_3OH, like that represented in Fig. 1c, but instead of going over the barrier to products, the reaction tunnels through it. The hydrogen-bonded complex sits in a relatively deep well on the potential surface such that its lifetime against redissociation to reagents becomes significantly longer at low temperatures, and this greatly increases the probability that the system will pass to products by tunnelling under the potential barrier.

The detection of CH_3O by Heard and colleagues provides a strong indication that the accelerated rate constant they observe is due to the mechanism described above. However, they are not able to measure an absolute yield of CH_3O product. Such a measurement would strengthen the case for the new mechanism. They did attempt measurements with deuterated methanol — the reduction in rate should be significant for tunnelling when the H atom is replaced by the heavier isotope — but they were unable to perform this key test owing to technical problems. An important next step would surely be to redesign the experimental apparatus and/or protocol to perform these measurements as a strong confirmation of the new result. It would also be most interesting to extend the measurements down to the actual temperatures of dense interstellar clouds (~10–20 K).

The role of weakly bound complexes in accelerating reactions at very low temperatures has been recognized for some time[7,8], but in the light of the two orders of magnitude acceleration observed, it is tempting to identify a completely new mechanism for H-atom transfer reactions involving hydrogen-bonded complexes in cold environments. It remains to be seen how many other reactions satisfy the rather nonlinear interplay between the stability of the complex with respect to falling apart to form the reagents and the probability of tunnelling through the barrier to give products. Furthermore, larger hydrogen-bonded addition complexes may be stabilized not only by collision with a third body, as might occur in a denser environment than interstellar clouds, but also by the emission of one or more infrared photons — so-called radiative association[9]. Such stabilization could reduce the impact of the new mechanism; however, it would result in the formation of new species of interest in their own right.

As well as being fascinating mechanistically, this research is also interesting from an astrochemical point of view. Recently, the CH_3O radical has been detected[10] by radio astronomy in B1-b — a cold, dense core within the dark interstellar cloud Barnard 1 — and as both OH radicals and methanol are relatively abundant in this cold environment, this research provides a completely new and plausible pathway to CH_3O. If the same mechanism can be shown to operate more generally for other reactions passing through hydrogen-bonded complexes, major improvements in models of cold interstellar clouds may result.

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