University of Canterbury

End-of-year Examinations 2009

Prescription Number(s):	CHEM 403 CHEM 415
Paper Title:	Chemical Dynamics and Spectroscopy Special Topic

Time Allowed:	TWO HOURS
Number of pages:	SIX

Answer **THREE** questions of out FOUR.

All questions are of equal value.

TURN OVER

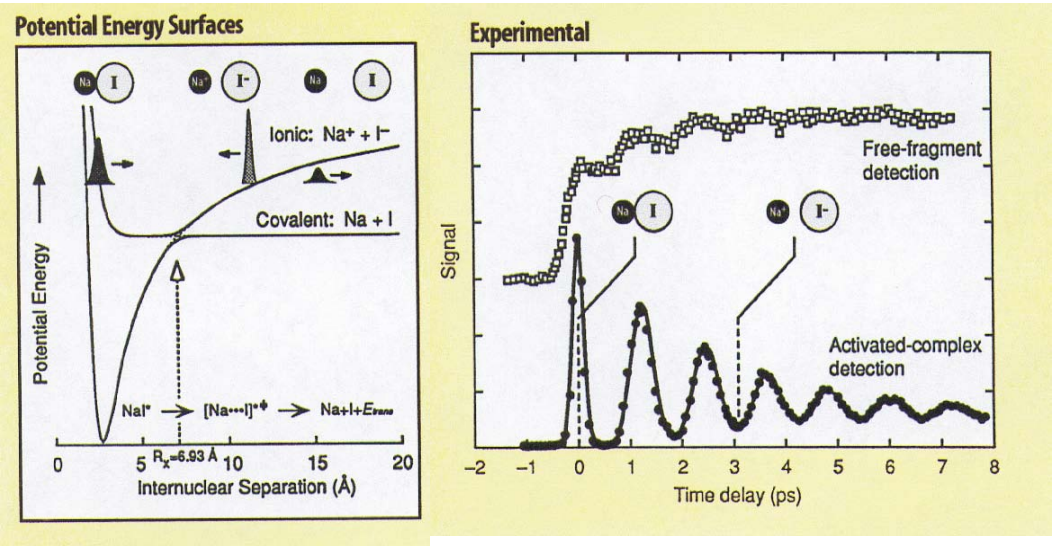
1. The harpoon or spectator-stripping mechanism for reactive collisions between electropositive projectiles and electronegative target molecules was initially suggested by M. Polanyi and co-workers in the 1940's following observations of reactions between Na atoms and a series of halogens and alkyl halides in a flow tube (sodium flame reactions) carried out in the 1930's.

(a) Using the reaction of Na (^{2}S) with Cl_2 X($^1\Sigma$) as an example, write chemical equations for the reactions taking place in the flow tube and explain how the results were interpreted by Polanyi *et al* in order to devise the harpoon or spectator stripping mechanism and to deduce details of the transition state species involved.

(b) The harpoon mechanism is described by Polanyi's Rules (John Polanyi, 1970's) as an attractive potential energy surface. Sketch a potential energy contour map for the Na (^{2}S) + Cl_2 X($^1\Sigma$) reaction, sketch a reaction trajectory on your diagram and explain the important features of such surfaces with reference to your answer to part a).

(c) v-t and r-t energy transfer and spontaneous relaxation of vibrational and rotational states are important considerations for kinetic studies in flow tubes operating under multiple collision conditions. Explain why this is the case and why they were not a significant factor in Polanyi's experiments.

(d) More recent investigations of the harpoon mechanism have been carried out by Zewail *et al*, J. Phys. Chem, A (2000) **104**, 5671. Using the potential energy surfaces shown in the left hand diagram below, interpret their experimental data, shown in the right hand diagram, in which femtosecond flash photolysis has been used to interrogate the dissociation of NaI^* on the same potential energy surfaces over which the reverse harpoon mechanism occurs.



2. Answer **two only** of the following.

(a) In an experimental cross-beam study of K(fast) + oriented $CH_3CN \rightarrow K^+ + CN^-$, CH_2CN^- by P. R. Brooks *et al*, J. Am. Chem. Soc., (2007) **129**, 15572, it was found that electron transfer from the K atom to CH_3CN to form CN^- is energy independent with only a small asymmetry favouring the CN-end of CH_3CN in contrast to CH_2CN^- formation which exhibits a strong preference for the positive end of the molecule at low collision energies which decreases with increasing energy.

Briefly explain:

(i) why fast K atoms are used and how they are generated;

(ii) how a beam of spatially oriented molecules are produced;

(iii) why collisions of fast K atoms with CH_3CN exhibit a high cross-section with no significant orientation dependence with G = 0.05 whereas in collisions of fast K atoms with CH_3Br there is a clear preference for forming the Br^- ion product at the Br-end of CH_3Br with a G value close to 0.40.

(iv) the difference between the stereodynamics of CN^- and CH_2CN^- formation in collisions of fast K atoms with CH_3CN.

(b) Ahmed Zewail (Nobel Prize 1999) has used femtosecond laser flash photolysis with femtosecond multi photon ionization (MPI) – time of flight mass spectrometry (TOFMS) to study a number of controversial reaction phenomena.

(i) Describe the technique of femtosecond laser flash photolysis –MPI TOFMS and explain why it is so versatile as a tool for investigating organic reaction mechanisms at the molecular level.

(ii) Explain how Zewail and co-workers determined whether nitrogen elimination in azomethanes was concerted or sequential.

(c) (i) Reaction of $H + Cl_2$ (v=0) $\rightarrow$ HCl + Cl occurs over a repulsive potential energy surface with the outcome modified by kinematics. Explain.

(ii) The reactions below yield bimodal triangle plots due to microscopic branching but the mechanisms involved are quite different. Explain.

$H + Cl_2$ (v=1) $\rightarrow$ HCl + Cl

$$H + ICl \rightarrow HCl + I.$$

3. The classical energy which describes the collision of two atoms in the centre of mass frame can be written as E:

$$E = \frac{1}{2\mu} p_r^2 + \frac{1}{2\mu r^2} p_\theta^2 + U(r) \quad , \qquad (1)$$

where

$$p_\theta = \mu v b \, . \qquad (2)$$

(a) Define, briefly, what each symbol in Equations (1) and (2) represents.

(b) Define the effective potential, U_{eff}, and sketch its shape for a typical atom-atom potential energy curve.

(c) What is the "deflection function"?

(d) For a typical atom-atom potential, sketch the shape of the deflection function as a function of the impact parameter.

(e) Write a formula for the classical differential cross section for elastic scattering of these two atoms.

(f) Assuming the deflection function sketched in (iv) above, sketch the classical differential cross section for elastic scattering as a function of the scattering angle.

4. For a chemical reaction, the dynamics can be strongly influenced by certain features of the molecular potential energy surface (PES).

(a) Define a "saddle point" on the PES.

(b) Define, qualitatively, what is a "minimum energy path" and how this might be calculated for a PES.

(c) In terms of a minimum energy path, what is the definition of a reaction coordinate?

(d) In a simple abstraction reaction, between an atom A and diatomic molecule, BC: $A + BC \rightarrow AB + C$, the forming AB bond and the breaking BC bond may be collinear on the minimum energy path and at the saddle point.

Describe Polanyi's rules for this reaction if the saddle point is "early" or "late". In doing so, give a reasoned qualitative description of how reactant translational energy and BC vibrational energy will influence the reaction probability in the two cases, and describe the probable distribution of energy in the products. Illustrate your answers with contour plots, energy profiles and idealised trajectories, as appropriate.

(e) Describe, briefly, what are the three main types of long range interactions between molecules.

END OF PAPER