

## ON THE DESORPTION KINETICS OF CHEMISORBED IODINE IN ELECTRON DONOR SOLVENTS

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It was shown that the desorption kinetics of chemisorbed iodine in electron donor solvents obeys an equation obtained by solving a set of first order rate laws expressing the energetic non-uniformity of the solid surface. Reference desorption activation energies were calculated and compared with the CT complex formation free energies.

### Introduction

Though kinetic studies of heterogeneous reactions, like isotope exchange, adsorption, desorption etc. have been frequently carried out, the lack of suitable methods for interpreting experimental data has been an important difficulty very often limiting the investigations merely to the phenomenology of the given process. Many systems were studied adapting the McKay equation, derived originally for homogeneous exchange kinetics, arbitrarily dividing the solid surface into a few types of surface sites required for the treatment of experimental data.

Recent studies led to the conclusion that instead of a few types of surface sites a great number of monoenergetic compartments has to be taken into account on an energetically non-uniform surface. Thus to interpret experimental data a great number of simultaneous heterogeneous processes has to be considered. The aim of this paper is to show that the desorption of a chemisorbed iodine monolayer in electron donor solvents occurs with the same kinetics as that of the heterogeneous isotope exchange governed by reaction at the solid-liquid interface rather than by diffusion. In interpreting the experimental results the equation obtained by solving a heterogeneous isotope exchange model with the aid of a computer programme was used.

### Experimental

Iodine monolayer labelled with  $^{131}\text{I}$  was formed on platinum rods (4-8 mm in length and 0.4 mm in diameter) according to a procedure described elsewhere.<sup>1</sup> Platinum rods carrying the iodine monolayer were brought into a U-shaped glass

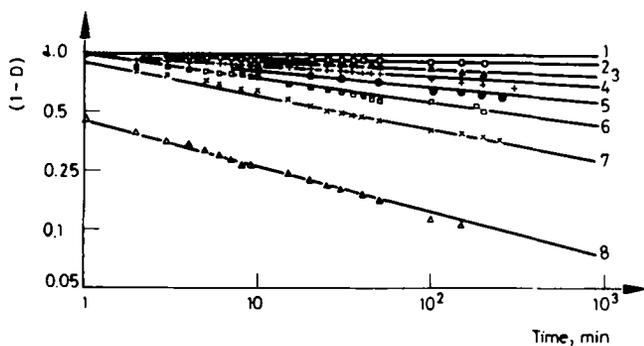
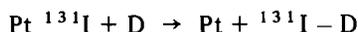


Fig. 1. Desorption fraction vs. time. Curves: 1 - n-heptane, 2 - ethyl ether, 3 - acetone, 4 - N-N'-dimethylaniline, 5 - ethanol, 6 - pyridine, 7 - n-butylamine

tube placed into a well-type NaI(Tl) scintillation crystal. The electron donor solvent passed through the tube removing the iodine desorbed according to reaction



where D - the electron donor solvent;

I-D - the CT complex formed between iodine and the solvent.

Since at time zero the radioiodine was entirely on the solid surface, the desorption rate could have been traced from zero time until the required time by counting  $^{131}\text{I}$  activity present in the well type crystal.

Parallel runs carried out with stirred and unstirred solvents showed that the liquid phase diffusion had no rate controlling effect.

The rate of desorption was expressed - on the analogy of isotope exchange - by the desorption fraction (1-D) which is defined as the ratio of the radioactivity present on the solid surface at time t divided by the initial activity:

$$(1 - D) = a_t/a_0$$

### Results and discussion

The (1 - D) values thus obtained were plotted against t in a lg - lg plot. Fig. 1 shows these plots for eight different electron donor solvents, while Fig. 2 presents the slope of the former plots vs. reciprocal temperature.

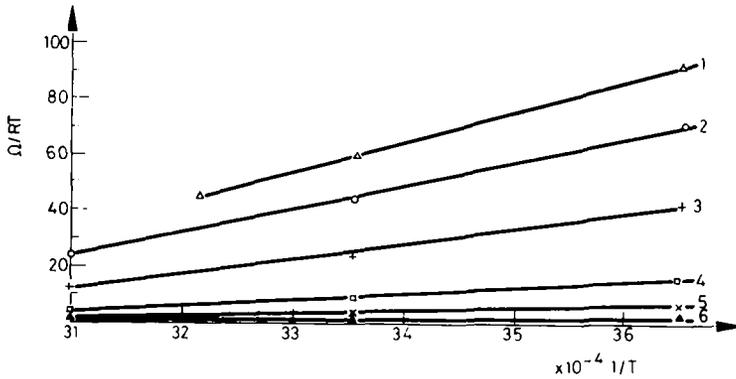


Fig. 2.  $\Omega/RT$  vs.  $1/T$ . Curves: 1 - ethyl ether, 2 - acetone, 3 - N-N'-dimethylaniline, 4 - pyridine, 5 - butylamine, 6 - piperidine

To interpret the experimental results shown in Figs 1 and 2 the equation expressing a linear relationship between  $\lg(1 - D)$  and  $\lg t$  was used. This equation was obtained for heterogeneous isotope exchange processes using the model as follows.<sup>2,3</sup>

It was considered that the solid surface is energetically non-uniform, i.e. the activation energy varies from surface site to surface site. No attempts were made to deal with the physical background of the surface heterogeneity, it should only be stressed that it is not the crystal morphology which is responsible for it. It was further supposed that the solid surface can be partitioned into a number of  $n$  compartments each compartment having the same number of surface sites and a constant activation energy belonging to each compartment:

$$E_1^* < E_2^* < E_3^* < \dots < E_n^*$$

where 1, 2, 3, ...  $n$  - indices mean the serial number of the monoenergetic compartments, while  $n$  is their total number.

For the distribution function expressing the activation energy dependence as a function of  $(1 - D)$  and/or  $i/n$  a logarithmic relation was chosen:

$$E_i = E_0 - \Omega \ln(1 - i/n) \quad (1)$$

which is in fact the Freundlich type energetic non-uniformity. From Eq. (1) and from the Arrhenius equation we obtain the distribution function of the first order rate constants:

$$k_i = k_0 (1 - i/n)^{\Omega/RT} \quad (2)$$

It can be shown that  $\Omega$  means the activation energy of the compartment which is to be found at 63% of the total number of compartments.

According to the kinetic model cited above the desorption fraction can be regarded as the resultant of  $n$  desorption fraction values each referring to a single monoenergetic compartment:

$$(1 - D) = \frac{1}{n} \sum (1 - D)_i \quad (3)$$

Taking into account that, since under the experimental conditions applied by us the desorption is a first order process, one has:

$$(1 - D)_i = -k_i t \quad (4)$$

the  $(1 - D)$  values can be calculated by solving  $n$  first order rate equations whose rate constants are defined by Eq. (2):

$$(1 - D) = \frac{1}{n} \sum_{i=0}^{i=n-1} e^{-k_i t} = \frac{1}{n} \sum_{i=0}^{i=n-1} e^{-k_0 \left(1 - \frac{i}{n}\right)^{\Omega/RT} t} \quad (5)$$

Since no exact solution for a set of equations like Eq. (5) exists, there are only two ways to calculate  $(1 - D)$ ; one of them is the use of an approximation as that of ROGINSKI and ATKINSON,<sup>4,5</sup> the other one is to solve the given system of equations numerically using a computer programme and to analyse the  $(1 - D)$  vs.  $t$  correlation thus obtained.<sup>2,3</sup>

It can be shown for  $n > 100$  and  $\Omega > 1 - 2$  the solution of Eq. (5) yields a linear  $\lg(1 - D)$  vs.  $\lg t$  relationship which is in agreement with the experimental results shown in Fig. 1:

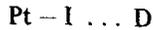
$$\ln(1 - D) = - \frac{RT}{\Omega} (\ln k_0 + \ln t) \quad (6)$$

According to Eq. (6) the slope is inversely proportional to  $\Omega$ , i.e. the reference activation energy. In Table 1 the reciprocal slopes, the  $\Omega$  values and the free energy of the given CT complex formation are listed.

Table 1  
Data characteristic for some CT complex formation

Electron donor solvent	$\Omega/RT$ (25 °C)	$\Omega$	$-\Delta G^\circ$ , kcal/mole
Ethyl ether	60	36	0.94
Acetone	43	26	0.92
N-N'-dimethylaniline	23	14	2.92
Pyridine	9	5.4	4.4
Butylamine	4.3	2.6	5.3
Piperidine	3.3	2.0	6.4

From the data listed in Table 1 the conclusion can be drawn that the higher the complex formation free energy the lower the activation energy necessary to the iodine desorption. This is in agreement with the supposed desorption mechanism according to which the first step is the formation of a transient complex.



which decomposes yielding the I-D CT complex. The higher the formation free energy of I-D the higher the probability of the rupture of the Pt-I bond.

Since the data shown in Table 1 express an almost linear relationship between  $1/\Omega$  and  $\Delta G$  the conclusion can be drawn that the kinetics of the desorption from an energetically non-uniform surface can be characterized by  $\Omega$ , i.e. by the activation energy of the monoenergetic compartment to be found at 63% of the total number of monoenergetic compartments. On the other hand, the linear  $\lg(1-D)$  vs.  $\lg t$  relationship stands for the Freundlich type energetic non-uniformity of the solid surface. It seems that the treatment of experimental data presented in this paper can be applied to other non-diffusion-controlled heterogeneous processes taking place on an energetically non-uniform solid surface.

### References

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