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On the Theory of Collision Desorption of Molecules from Solid Surfaces

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An experimental result, that the activation energy of the catalytic chemical reaction $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$ at a V_2O_5 surface depends on the gases used to dilute the reactants, led Baron, Manning and Johnstone (BMJ, *Chem. Eng. Progr.* **48**, 125 (1952)) to propose that, in this reaction, the desorption of SO_3 may be the rate-controlling step, and that this desorption may be caused more by collisions with the adsorbed SO_3 molecules of molecules from the gas phase than by a thermal desorption process. BMJ's results are corrected and rederived in a more modern terminology, using the concept of the energy accommodation coefficient. It is assumed that the probability rate, ν, for thermal desorption obeys the well-known Frenkel formula, $\nu = \nu_0 \exp(-D/kT_s)$ in a standard notation, and it is further assumed that ν_0 has its usual value of about 6×10^{12} sec^{-1}. With these assumptions, the expected rates of collision desorption and thermal desorption are compared, and it is concluded that collision desorption is negligible in the relevant experiments; this conclusion substantiates that of Yeramian, Silveston, and Hudgins (*Can. J. Chem.* **48**, 1175 (1970)), who concluded that the experimental data are inconsistent with the BMJ model of collision desorption.

INTRODUCTION

Baron, Manning and Johnstone (BMJ) (*1*) discovered that the activation energy for the oxidation of SO_2 over a V_2O_5 catalyst (the net result of which is $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$) depends on the gas used to dilute the reactants; this "diluent-gas effect" in this catalytic reaction has been confirmed by Yeramian, Silveston and Hudgins (*2*). In order to give a qualitative explanation of this diluent-gas effect, BMJ proposed that (a) SO_3 is formed from SO_2 and $\frac{1}{2}O_2$ on the V_2O_5 surface relatively quickly, (b) the subsequent desorption of SO_3 is the rate-controlling (slowest) step in the overall reaction, and (c) this desorption is caused more by collisions with the adsorbed SO_3 molecules of molecules from the gas phase than by an ordinary thermal desorption process, because thermal desorption is usually associated with a *constant* activation energy. We assume that the probability rate, ν, for thermal desorption (that is, for the process surface + adsorbed SO_3 → surface + desorbed SO_3) obeys the well-known Frenkel formula

$$\nu = \nu_0 \exp(-D/kT_s), \tag{1}$$

where k is the Boltzmann constant, ν_0 is a characteristic vibration frequency of the adsorbed molecules (*3*,*4*), T_s is the temperature of the surface, and D is the (constant) activation energy.

As is shown below, the theory of collision desorption leads to an apparent activation energy for desorption which depends on the translational energy accommodation coefficient (denoted by EAC, or simply by α) of the system comprising the molecules in the gas phase and the adsorbed molecules, and hence depends on the molecules in the gas phase. The definition of α is (*5*)

$$\bar{E}_0 - \bar{E}_1 = \alpha(\bar{E}_0 - \bar{E}_s), \tag{2}$$

where $\bar{E}_0$ and $\bar{E}_1$ are the average incident and scattered translational energies, respectively, of the gas molecules and E_s is the value of $\bar{E}_1$ for molecules scattered in thermal equilibrium with the surface:

$$E_s = 2kT_s. \qquad (3)$$

For the particular case where the incident gas molecules have a velocity distribution corresponding to thermal equilibrium at temperature, T_g, the definition (2) may be written

$$T_g - \bar{E}_1/2k = \alpha(T_g - T_s). \qquad (4)$$

MODEL FOR COLLISION DESORPTION

We let ξ be the number rate of gas molecules incident per unit area of surface, given from the kinetic theory by

$$\xi = p(2\pi M_g kT_g)^{-1/2}, \qquad (5)$$

where p is the gas pressure and M_g the gas molecular mass. We let θ be an effective fractional surface coverage by adsorbed molecules (equivalent to BMJ's $p\theta\pi S_{AB}{}^2$); where $N(E_0)$ is the number rate, per unit area of surface, of incident gas molecules striking adsorbed molecules, we have, also from the kinetic theory,

$$\frac{dN}{dE_0} = \theta\xi \frac{E_0}{(kT_g)^2} \exp\left(-\frac{E_0}{kT_g}\right). \qquad (6)$$

As a check on (6), we observe that

$$N = \int_0^\infty \frac{dN}{dE_0}\, dE_0 = \theta\xi, \qquad (7)$$

which is correct by definition of θ and ξ. Our (6) should be equivalent to BMJ's equation (8), after correcting the obvious printer's error (S_{AB} should be $S_{AB}{}^2$) therein; however, their equation contains an extra factor of 4, the origin of which the author does not understand.

We assume that the gas and adsorbed molecules may be regarded as spheres, of radii r_g and r_a, respectively, and that an incident gas molecule may strike an adsorbed molecule with any geometry; that is, representing the incident molecule by a point particle and the adsorbed molecule by a sphere of radius $R = r_g + r_s$, we assume that the incident gas molecule trajectories (Fig. 1) are distributed uniformly over the appropriate circle of radius R (R is equivalent to BMJ's S_{AB}). When estimating the contribution to desorption of the collision desorption mechanism, we eliminate the possibility of thermal desorption by assuming that the adsorbed molecule is initially stationary; a collision is assumed to be "successful," or to be a "desorbing collision," if the energy transfer, $E_0 - E_1$, to the adsorbed molecules exceeds D:

$$\text{desorbing collision:} \quad E_0 - E_1 > D. \qquad (8)$$

In Fig. 1, ψ (equivalent to BMJ's γ) is the angle between the line of centres of the two molecules at collision and the velocity vector, v_0, of the incident gas molecule. The distribution function of ψ is denoted by $\Psi(\psi)$ and, with the above assumptions about the distribution of the incident gas molecule trajectories, it is easy to show that

$$\Psi(\psi) = \sin(2\psi): \quad 0 < \psi < \pi/2. \qquad (9)$$

The distribution $\Psi(\psi) = \sin\psi$ used by BMJ is incorrect. Hence, the joint distribu-

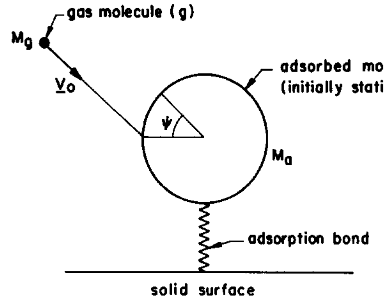

FIG. 1. Model for collision desorption. Desorption of a is assumed to occur if the translational energy transfer from g to a during the collision exceeds the activation energy for desorption. The mass ratio μ is M_g/M_a.

tion of E_0 and ψ is the product of (6) and (9):

$$\frac{d^2N}{dE_0 d\psi} = \frac{\theta\xi E_0 \sin(2\psi)}{(kT_g)^2} \exp\left(-\frac{E_0}{kT_g}\right). \quad (10)$$

Assuming that the gas and adsorbed molecules interact as though they were hard spheres, it is easy to show that, for the geometry in Fig. 1,

$$E_0 - E_1 = E_0 \alpha_0 \cos^2\psi, \quad (11)$$

where α_0 is defined by

$$\alpha_0 = 4\mu/(1+\mu)^2 \quad (12)$$

and μ is the mass ratio, defined by

$$\mu = M_g/M_a, \quad (13)$$

where M_a is the adsorbed molecular mass. The assumption of an initially stationary adsorbed molecule implies the assumption that $T_s = 0$, and it follows from (3), (9), (11) and (12) that the EAC is given by

$$\alpha = \alpha_0 \int_0^{\pi/2} \cos^2\psi \sin(2\psi) d\psi = \frac{1}{2}\alpha_0. \quad (14)$$

(In passing, we may note that this value of α is, in fact, the well-known "Baule" EAC (*6*,*5*).) We note, for future reference, the inherent restriction on α which follows from (12) and (14):

$$2\alpha \leq 1. \quad (15)$$

It follows from (14) that we may write (11) in terms of α as follows:

$$E_0 - E_1 = 2E_0\alpha \cos^2\psi. \quad (16)$$

Further, the condition (8) may be written

desorbing collision: $2\alpha E_0 \cos^2\psi > D$. (17)

We define λ_c as the number rate of desorbing collisions, per unit area of surface, and it follows from (10) and (17) that

$$\begin{aligned}\lambda_c &= \int_{(2\alpha E_0 \cos^2\Psi > D)} dE_0 \int d\psi \, d^2N/dE_0 d\psi \\ &= \frac{\theta\xi}{(kT_g)^2} \int_0^{\pi/2} \sin(2\psi) d\psi \\ &\quad \times \int_{D/2\alpha\cos^2\psi}^{\infty} E_0 \exp\left(-\frac{E_0}{kT_g}\right) dE_0 \\ &= \theta\xi \exp(-D/2\alpha kT_g). \quad (18)\end{aligned}$$

Apart from the factor of 4 mentioned above, (18) is the same as BMJ's equation (17), without their second (erfc) term, and, again apart from the factor of 4, (18) is the same as their "approximate" equation (20). Thus we see that the result of using the incorrect $\Psi(\psi) = \sin\psi$, as done by BMJ, is the appearance of the second (erfc) term in their equation (17). [Use of $\Psi(\psi) = \sin\psi$ instead of (9) leads to the following equation in place of (18):

$$\lambda_c = \theta\xi \left[\exp\left(-\frac{D}{2\alpha kT_g}\right) - \frac{\pi^{1/2} D}{4\alpha kT_g} \operatorname{erfc}\left(\frac{D}{2\alpha kT_g}\right)\right], \quad (19)$$

which, again apart from the factor of 4, is the same as BMJ's equation (17).]

The analog of λ_c for thermal desorption, in the absence of collisions, is denoted by λ_t and is given by $\rho\nu$, where ρ is the number of adsorbed molecules per unit area and ν is given by (1)

$$\lambda_t = \rho\nu_0 \exp(-D/kT_s). \quad (20)$$

An effective cross-section, σ, for a collision between an incident gas molecule and an adsorbed molecule is defined by

$$\theta = \rho\sigma; \quad (21)$$

thus ρ corresponds to BMJ's θ and σ to BMJ's $P\pi S_{AB}{}^2$. It follows from (18) and (20) that the ratio of the rates of collision desorption (in the absence of thermal desorption) and thermal desorption (in the absence of collision desorption) is given by

$$\frac{\lambda_c}{\lambda_t} = \frac{\sigma\xi}{\nu_0} \exp\left(\frac{D}{kT_g}\left(\frac{T_g}{T_s} - \frac{1}{2\alpha}\right)\right). \quad (22)$$

Orders of magnitude for σ and ν_0 are obtained as follows: $\sigma \approx \pi R^2$, where R is the hard-spheres interaction radius, and

$R \approx 3A$ leads to

$$\sigma \approx 30A^2; \tag{23}$$

ν_0 may be written

$$\mathrm{N}_0 \,/\, K\Theta/2\pi\hbar$$

as usual, where $2\pi\hbar$ is the Planck constant and Θ is a characteristic vibration temperature, of order 300 K, leading to

$$\nu_0 \approx 6 \times 10^{12}\ \mathrm{sec}^{-1}. \tag{24}$$

It follows from (5) that ξ may be written in the form

$$\xi \approx \frac{10^5 p}{A^2 \mathrm{sec\ Torr}} \left(\frac{4\ \mathrm{amu}}{M_g} \frac{300\ \mathrm{K}}{T_g} \right)^{1/2}, \tag{25}$$

and hence

$$\frac{\lambda_c}{\lambda_t} \approx 5 \times 10^{-7} \frac{p}{\mathrm{Torr}} \left(\frac{4\ \mathrm{amu}}{M_g} \frac{300\ \mathrm{K}}{T_g} \right)^{1/2} \times \exp\left(\frac{D}{kT_g} \left(\frac{T_g}{T_s} - \frac{1}{2\alpha} \right) \right). \tag{26}$$

APPLICATION OF THE MODEL TO PRESENT EXPERIMENTS

In the experiments under consideration (1,2) $T_s = T_g = T$, for which case (26) specializes to

$$\frac{\lambda_c}{\lambda_t} \approx 5 \times 10^{-7} \frac{p}{\mathrm{Torr}} \left(\frac{4\ \mathrm{amu}}{M_g} \frac{300\ \mathrm{K}}{T} \right)^{1/2} \exp\left(-\frac{D}{kT} \left(\frac{1 - 2\alpha}{2\alpha} \right) \right). \tag{27}$$

An important conclusion follows from (27), and that is that the collision desorption process is almost certain to be neglible under these conditions ($T_s = T_g = T$) because of the restriction (15), which implies that the exponent in (27) is never positive. For example, taking the extreme (and best for collision desorption) case $2\alpha = 1$, for He gas at $T = 300$ K we obtain $\lambda_c/\lambda_t \approx 4 \times 10^{-4}$ even if $p = 1$ atm; similar conclusions are reached for all the experimental systems in Refs. (*1*) and (*2*). We must, therefore, conclude that, if the assumptions made in this paper are correct, collision desorption is negligible in these experiments (*1,2*), and that some other phenomena are responsible for the apparently anomalous results. The authors of Ref. (*2*) concluded that the experimental data are inconsistent with the model (*1*) of collision desorption, and our conclusion substantiates theirs.

THE CASE OF COMPLETE ACCOMMODATION

The model described so far contains the inherent restriction (15) on α, thus excluding the case $\alpha > 0.5$. That this sort of restriction must be present in such a model is clear, because the model was constructed (*1*) to explain a dependence of activation energies on the gases used as diluents, which dependence was thought to be a mass effect. The hard spheres model gives the most extreme mass effect possible (if $\alpha \approx 1$ there can be essentially no dependence of α on any parameter). Nevertheless, it may appear at first sight as though the possibility of $\alpha > 0.5$ may negate the conclusions made just after (27) because of the form of the exponent therein.

However, it must be borne in mind that, if $\alpha > 0.5$ is allowed, then (27) must be rederived with new assumptions; for example, it would be wrong to substitute any value of $\alpha > 0.5$ in (27). Taking $T_s = 0$ (remember that we take $T_s = 0$ when calculating λ_c) and the extreme case of complete accommodation, $\alpha = 1$, for simplicity, it follows from (2) and (3) that $E_1 = 0$ and hence that (8) must be changed to read as follows:

$$\text{desorbing collision } (\alpha = 1){:}\ E_0 > D. \tag{8$'$}$$

Accordingly, (18) is changed as follows:

$$\begin{aligned} \lambda_c &= \int_{(E_0>D)} dE_0 \int d\psi\, d^2N/dE_0 d\psi \\ &= \theta\xi/(kT_g)^2 \int_D^\infty E_0 \exp\,(-E_0/kT_g) dE_0 \\ &= \theta\xi(1 + D/kT_g) \exp\,(-D/kT_g). \end{aligned} \tag{18$'$}$$

The end result is that (27) now reads

$$\frac{\lambda_c}{\lambda_t} \approx 5 \times 10^{-7} \frac{p}{\text{Torr}} \left(\frac{4 \text{ amu}}{M_g} \frac{300 \text{ K}}{T} \right)^{1/2} \left(1 + \frac{503D}{T} \frac{\text{mole K}}{\text{kcal}} \right). \quad (27')$$

All the values of D considered in Ref. (*2*) obey $D < 40$ kcal mole^{-1}; therefore, again for He gas at $T = 300$ K, we obtain $\lambda_c/\lambda_t < \sim 0.025$ if $p = 1$ atm. Further, it would be no use trying to enhance the effect of collision desorption by choosing systems with values of D/T large enough to make $\lambda_c/\lambda_t > 1$ in (27′), because then thermal desorption and collision desorption would be separately negligible on account of the exponents in (20) and (18′), respectively. Therefore, the conclusion that collision desorption is negligible in the types of experiment under consideration is independent of the value assumed for α.

CONCLUDING REMARKS

For a given gas-surface system, the relative effect of collision desorption would be enhanced by either (a) inhibiting thermal desorption while keeping the incident gas energy constant (that is, lowering T_s below T_g) or (b) increasing the collision frequency (that is, increasing p); this fact is clear from the form of (26). However, it is not yet possible experimentally to lower T_s below T_g for a sufficiently long period, and it is difficult to see how this will ever be possible (unless, perhaps, p is small, which would defeat the object of the exercise). In the author's opinion, the only conditions under which collision desorption will be important are those in which the incident gas molecules form a molecular beam, the point being that the incident gas energy is then not coupled to T_s. It would then be possible to lower T_s independently of other parameters and thus to inhibit thermal desorption, when collision desorption may become important; indeed, in a molecular beam experiment, collisions may dominate even at quite large T_s if D is sufficiently large.

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