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The Role of Heterogeneity in the Kinetics of a Surface Reaction

III. Distributions in Activation Enthalpy and Entropy[1]

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On the basis of the experimental data presented in the two foregoing papers of this series the following subjects are now treated. (i) The activation free energy distribution is directly derived from the experimental results. Moreover, the separate contributions of enthalpy and entropy of activation are calculated. (ii) The large discrepancy between the experimental frequency factor and the one that follows from the absolute rate theory is explained tentatively by questioning the basic equilibrium hypothesis of the theory. (iii) Those surface properties which ultimately give rise to the variation in activation free energy are discussed.

INTRODUCTION

An infrared study has identified the decomposition reaction of isopropyl methylphosphonofluoridate (sarin) adsorbed on alumina or magnesia (*1*a); the reaction products are isopropyl methylphosphonic acid and hydrogen fluoride, which are also adsorbed. The kinetics of this surface reaction, which have been studied microcalorimetrically (*1*b), revealed that the Zeldovich rate equation provides a sound basis for a description of the experimental rate data [see also the foregoing papers of this series (*2*)]. A model that is able to explain the experimental reaction rates has been described (*1*b). Reference may also be made to the previous parts of this series (*2*a, b).

The primary characteristic of this model is a distribution in activation free energy for the defluoridation reaction; a rectangular distribution function (i.e., a function which is constant between two energy values and zero outside that interval) appears to be consistent with the experimental results.

With respect to catalyzed reactions, Constable (*3*) was the first to recognize and to describe the influence of a distribution in activation energy on the rate. Starting from a statistical formulation of the strain energies between surface atoms, he arrived at an exponential distribution of the activation energies. Unlike Constable (*3*), Halsey (*4*) incorporated the possibility that the rate limiting step of the catalyzed reaction is different on different sites. He concluded that the shape of the distribution is relatively unimportant, provided it is broad. Roginskii (*5*) showed for a number of arbitrarily chosen distribution functions that the largest rate constant largely determines the catalytic activity provided again the distribution is broad. Experimental evidence for definite distributions in activation energies for catalyzed reactions seems to be completely lacking (*6*).

The influence of a varying activation energy on the kinetics of the present

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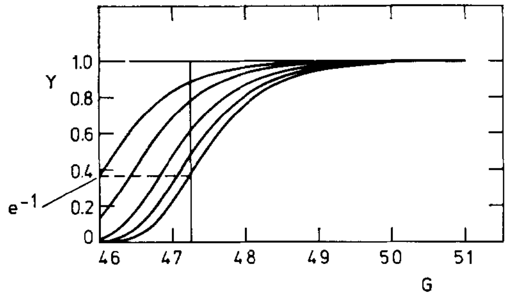

FIG. 1. Illustration of Eq. (1) for $T = 300°K$; t equals, respectively, 1, 4, 7, 10, and 13 sec. Roginskii (*5*) replaces each sigmoidal curve by a vertical through the inflexion point; this is illustrated for $t = 13$ sec.

reaction, however, is less complex than on a catalyzed reaction; the differently active sites operate only once, whereas in catalytic processes all sites are active continually. In this respect the sarin decomposition is identical to chemisorption and desorption processes, where sites are operative only once as well. In these cases activation energy distribution functions may be calculated from experimental rate data. Only a few such distributions are known from the literature (*7*, *8*).

In this paper a calculation procedure developed by Roginskii (*5*) will be used in an extended form, enabling us to derive the distribution activation free energies. Computation of the separate entropy and enthalpy components of the activation free energy is made possible.

DISCUSSION

Distribution Function

The block-shaped function which was postulated before and which described the experimental results satisfactorily, may for a substantial part be derived directly from the experimental data.

Roginskii (*5*) devised a method to relate the rate of chemisorption and desorption processes to underlying variations in activation energies. Although in his procedure the frequency factor is assumed to be constant and the activation enthalpy is the only variable, his method is applicable equally well when the activation free energy is assumed to be variable.

The calculation will be shortly revived here by applying it to the reaction system sarin–adsorbent; decomposition replaces chemisorption. At time $t = 0$ an amount of sarin is divided over a set of adsorption sites that show a distribution in activation free energy for defluoridation [$\rho(G)$] between the limits G_1 and G_2. The extremes of the reaction rate constants are determined by the relations $k_1 = (k_bT/h)\exp(-G_1/RT)$ and $k_2 = (k_bT/h)\exp(-G_2/RT)$. For a definite value of G the sarin molecules decompose according to first order kinetics; at time t the remaining fraction of sarin at the ensemble of sites characterized by G equals:

$$\gamma(G,t) = \exp(-k_Gt).$$

Because $k_G = (k_bT/h)\exp(-G/RT)$ it is valid that

$$\gamma(G,t) = \exp\{-k_0't\exp(-G/RT)\}, \qquad (1)$$

where k_0' stands for k_bT/h.

Graphical representation of the expression for a number of equidistant values of t leads to a collection of congruent sigmoidal curves, as shown in Fig. 1. The area between subsequent curves is proportional to the quantity of sarin decomposed in the related period.

The relative reaction rate in a small interval ΔG around G is defined by $[-(d\gamma/dt)]_G\Delta G$. The absolute rate is found by multiplying this quantity by the value of the distribution function at G:

$$r_G(t) = \left(-\frac{d\gamma}{dt}\right)_G \rho(G)\Delta G.$$

The total rate follows by integrating r_G between the limits of G:

$$r(t) = \int_{G_1}^{G_2} -\left(\frac{d\gamma}{dt}\right)\rho(G)dG.$$

Although $d\gamma/dt$ may be written as a function of G by means of Eq. (1), the solution of $\rho(G)$ from the resulting equation is very complex.

Roginskii greatly simplified the problem by simulating that the molecules react in an order of increasing activation free energy; this means that the sigmoidal curve of Fig. 1 is replaced by a vertical front. This approach implies that the finally calculated distribution function becomes approximative in that the different energies are "scrambled." It may be calculated, however, that 90% of the molecules reacting in a short time interval are contained in a G interval of 1.9 kcal/mole width (*1*b). Roginskii somewhat arbitrarily chose the average G value in the inflexion point of the sigmoidal curve. (A more precise treatment shows that the position of the real average differs by only a few tenths of a kilocalorie per mole from the inflexion point.) The position of the inflexion point is found by differentiating Eq. (1) twice:

$$G_{ip} = RT \ln (k_bT/h)t. \qquad (2)$$

An explicit expression for the distribution function $\rho(G)$ is found as follows. The amount of decomposed sarin at time t corresponding to the G value of Eq. (2) is given by

$$\phi\{G(t)\} = \int_{G_1}^{G(t)} (1 - \gamma)\rho(G)dG. \qquad (3)$$

As the sigmoidal curves are approximated by verticals, $(1 - \gamma)$ must be set equal to unity for $G < G(t)$. Hence Eq. (3) transforms to:

$$\phi\{G(t)\} = \int_{G_1}^{G(t)} \rho(G)dG.$$

ϕ may be differentiated with regard to G:

$$\frac{d\phi}{dG} = \rho(G).$$

Differentiating Eq. (2) leads to

$$\frac{dG}{dt} = \frac{RT}{t}.$$

Realizing that

$$\frac{d\phi}{dt} = \frac{d\phi}{dG}\cdot\frac{dG}{dt},$$

it follows that the total reaction rate may be written as:

$$r \equiv \frac{d\phi}{dt} = \frac{RT}{t}\rho(t).$$

Consequently, according to Roginskii, the distribution may be expressed purely in terms of the measured quantities r and t:

$$\rho(t) = \frac{rt}{RT}. \qquad (4)$$

Combination of Eq. (4) with the relation $G = RT \ln (k_bT/h)t$ enables one to represent ρ as a function of G; a plot of rt/RT vs $\ln t$ visualizes this representation.

In order to illustrate the applicability of the method, a few artificial distributions are worked out here. Each distribution is composed of n sets of identical sites while each set has an initial concentration c_i^0. Within every set G is constant, while the sets are separated by equal intervals ΔG. For such distributions the total reaction rate is given by:

$$r = \sum_{i=0}^{n} c_i^0 k_i e^{-k_it}. \qquad (5)$$

In the first example all c_i^0 are taken unity, $n = 8$ and $k_i = (k_bT/b) \exp\{-(G_0 + iRT)/RT\}$ with $k_0^1 = 150$ s^{-1} and $G_0 = 41.7$ kcal/mole. The corresponding distribution function is illustrated in the bar chart of Fig. 2. The graphical representation of $\rho(G)$ as defined above is shown in Fig. 2. As was expected, the calculated distribution has been smoothed. When a similar distribution function, differing from the former by an interval width of 2 RT instead

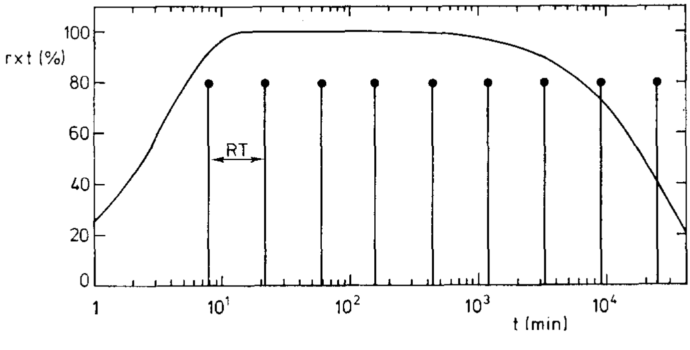

FIG. 2. (⚲) Bar chart of an activation free energy distribution given by Eq. (5) for $n = 8$, $G_0 = 41.7$ kcal/mole and $c_i^0 = 1$. The curve is a representation of the same distribution calculated from the kinetic data of a fictitious experiment. The largest $r \times t$ value is taken as 100%.

of RT (see bar chart in Fig. 3) is treated in the same way, the curve of Fig. 3 is obtained. The spacing of $2RT$ is clearly recognized in the results obtained from the fictitious experiment. Figure 4 shows the resemblance between a Gaussian shaped distribution function and the representation calculated from the fictitious kinetic experiment. The shape of the function is largely preserved, although the calculated representation is slightly broadened relative to the real distribution.

These examples show the usefulness of the calculation method. By applying the procedure to the experimental results of the sarin decomposition on alumina (the product $r \times t$ is constant in the period from 40 to 3000 min or more) it may be concluded that the energy distribution function is constant over an interval of at least $RT \ln (3000/40) \simeq 3$ kcal/mole.

Activation Enthalpy and Entropy

The activation free energy of a reaction comprises an enthalpy and an entropy component:

$$G = \Delta H_{\text{act}} - T\Delta S_{\text{act}}.$$

The question to be answered here is how much enthalpy and entropy elements contribute separately to the activation free energies for sarin defluoridation. Correlations between activation entropy and enthalpy have been observed to exist for catalytic reactions. When a definite re-

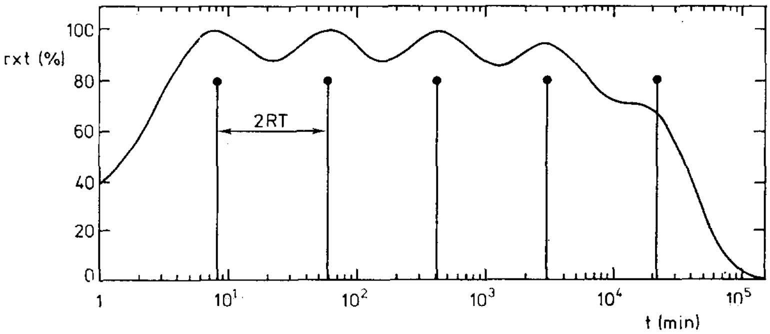

FIG. 3. (⚲) Bar chart of an activation free energy distribution given by Eq. (5) for $n = 5$, $G_0 = 41.7$ kcal/mole and $c_i^0 = 1$; the spacing between subsequent levels has been taken as $2\ RT$. The curve represents the same distribution calculated from the kinetic data of a fictitious experiment.

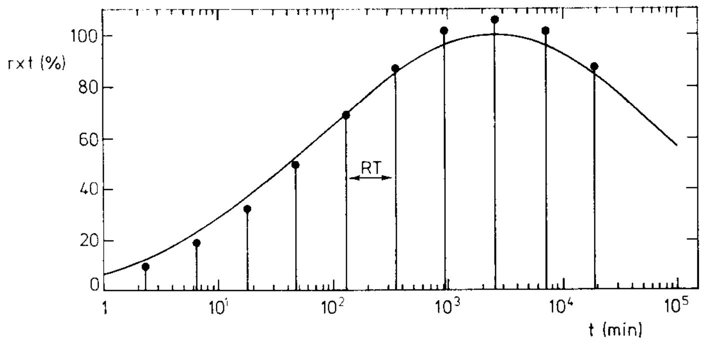

FIG. 4. (⫯) Bar chart of an activation free energy distribution with Gaussian character. The curve represents the same distribution calculated from the kinetic data of a fictitious experiment.

action proceeds over a series of analogous catalysts the relation between $\ln k_0$ and ΔH_{act} is often found to be linear on the understanding that the effect of a decrease of activation energy is (partly) annihilated by a decrease of the frequency factor. This phenomenon, known as the compensation effect, has been interpreted in various ways (see, e.g., Refs. *9, 10*) but no explanation has general validity.

Results similar to those characterized by the compensation effect have been reported by Brundege and Parravano (*7*). These authors studied the exchange between benzene adsorbed on platinum black and gaseous benzene, using a kinetic isotopic method. The surface sites that were actually involved in the exchange reaction comprised about 5% of the surface area. A broad scatter in activation energy as well as in frequency factor was found: the activation energy varied from 10 to 35 kcal/mole, while the range of the frequency factor was 10^7 to 10^{26} min^{-1}. The relation between $\ln k_0$ and E_{act} was linear, as is often found for one reaction proceeding on a series of related catalysts. The differential distribution in activation energies appeared to be rectangular. The calculation procedure followed by Brundege and Parravano to arrive at distribution functions of ΔH_{act} and ΔS_{act} is not general. They tacitly assume that the reaction rate constant decreases monotonically with E. This assumption implies that the term $k_0(E)$ in the expression for the reaction rate constant,

$$k = k_0(E) \exp(-E/RT),$$

is subjected to an a priori restriction, which was not justified. No conclusions concerning the mechanistic causes of the variation in E and k_0 could be drawn, because the reaction mechanism was not known.

Another example of activation energy distribution is available in the literature. Chornet and Coughlin (*8*) described the desorption kinetics of hydrogen chemisorbed at 298°K on polycrystalline iron; desorption temperatures lay in the range of 370 to 550°K. The activation energy for desorption showed a more or less homogeneous distribution between 13 and 20 kcal/mole. A linear relation between $\ln k_0$ and ΔH_{act} holds for this reaction also. On the basis of a mobile adsorption Chornet and Coughlin argue that the desorption kinetics are compatible with a model adopting (i) a homogeneous surface and (ii) changes in hydrogen atom activity on account of variation in mutual lateral interactions. Lateral interactions do not obscure the picture of Brundege and Parravano, because the surface coverage of their adsorbent was constant during an experiment, while it was assumed to be equal in the series of reactions at various temperatures. Therefore, the variations in ΔH_{act} and k_0 are to be ascribed to surface

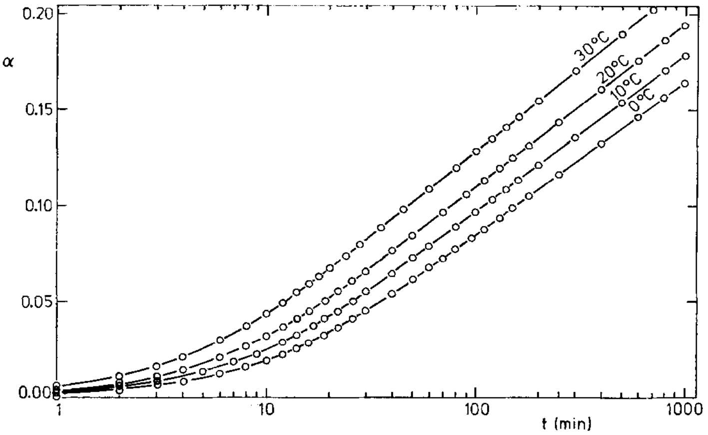

FIG. 5. Sarin decomposition on Ketjen alumina pretreated at 120°C. Fraction of decomposed sarin vs log t for different reaction temperatures; α is calculated from experimental results by means of Eq. (6).

inhomogeneity exclusively, under the sole condition that the distribution over the different sites is temperature independent.

The defluoridation reaction of adsorbed sarin is comparable to the two examples given above, in that a distribution in activation free energy is measured for a single reaction on one adsorbent.

The activation enthalpy and entropy of the defluoridation reaction are calculated by constructing Arrhenius plots for each fraction of molecules characterized by one definite activation free energy. The method is illustrated by Figs. 5 and 6.

Figure 5 shows the fraction of decomposed sarin as a function of log t. (Note the straight sections in the curves, indicating the adherence to Zeldovich kinetics.) The curves have been obtained by integrating the reaction rate between 0 and t [see Part II of this series (*2*b)]:

$$\alpha(t) = \int_0^t \frac{RTC^0}{G_2 - G_1}\frac{1}{t'}\{1 - \exp(-k_1 t')\}dt'. \tag{6}$$

The values for $RTC^0/(G_2 - G_1)$ and k_1 were taken from data presented in the previous paper (*2*b); for the reaction enthalpy the calibrated value of 72 kcal/mole was assumed. At one definite value of α the same fraction of molecules is reacting for all temperatures, though at different times. These times may be related to the average reaction rate constants operative on those times. The reaction rate constant k may be written as:

$$\ln k = \ln\frac{k_b T}{h} - \frac{G}{RT}.$$

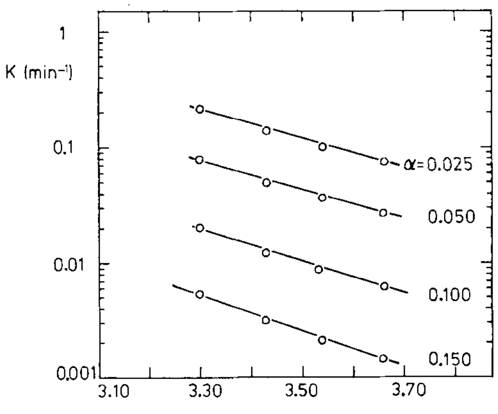

FIG. 6. Reaction rate constant as a function of reciprocal temperature for various fractions of decomposed sarin (α).

Comparison with Eq. (2) expressed as:

$$\ln t = -\ln\frac{k_b T}{h} + \frac{G}{RT},$$

reveals that the reciprocal time gives the (av) value of the rate constant of the molecules reacting at this time. For a few values of α the corresponding k values at the four experimental temperatures have been plotted in the Arrhenius graphs of Fig. 6; from each best fitting straight line an activation enthalpy and entropy related to the same α, may be calculated. Figure 7 shows the dependence of both ΔH_{act} and $\ln k_0$ on the degree of conversion. ΔH_{act} increases linearly with α, whereas $\ln k_0$ is virtually constant ($k_0 \simeq 2\ \text{sec}^{-1}$). Apparently the rectangular distribution of the activation free energy is to be found in a variation of the activation enthalpy. Evidently a compensation effect is absent.

Frequency Factor

In the preceding section it appeared that the experimental frequency factor equals 2 sec^{-1}. By writing the factor as:

$$k_0 = \frac{k_b T}{h} e^{\Delta S^\ddagger / R},$$

it is calculated from the rate constant and the experimental activation energy that $\Delta S^\ddagger$ amounts to -57 cal/mole °C (or e.u.). The reacting species are adsorbed in an immobilized state and cannot lose translational degrees of freedom. The entropy decrease has to be explained, therefore, from rotational and vibrational entropy losses.

Contribution to activation entropy by the adsorbent lattice is probable but cannot be quantified, not even roughly because nothing is known about the number of lattice ions potentially participating in (or influencing) the surface reaction. The very wide ranges of k_0 and E_{act} found for reactions on series of related catalysts might indicate that the actual lattice is strongly involved in the formation of the activated complex. Variations in k_0 of the order of 10^7 are quite regular, while even factors 10^{10} and 10^{19} have been reported [see the review by Cremer (*9*)]. For this reason large contributions of the adsorbent lattice to the activation entropy cannot be precluded, although no quantitative estimation can be made.

Loss of rotation of the two species involved in the rate limiting step (hydroxyl and sarin) can account for a contribution to the activation entropy of about 10 e.u., 1.9 e.u. for a hydroxyl (*11*) and 8.1 e.u. for a sarin molecule that is adsorbed immobile along the P=O axis. (The S_{rot} for sarin was calculated according to Halford (*12*) from a value of the momentum of inertia estimated from bond distances and ligand masses). So a large discrepancy remains, which can only be explained by loss of vibrational entropy. Except from the lattice, this loss may originate from the reaction species.

From the literature some examples are known of molecular groups that, although not directly involved in a chemical reaction, have an influence on the activation entropy of that reaction. Larsson (*13*) measured activation enthalpies and entropies for the hydrolysis in aqueous solution of two series of homologous alkyl-alkylphosphonofluoridates. It appeared that the activation entropy decreased (k_0 smaller) with increasing size of the alkyl group, while the activation energy was constant in a series.

Taft (*14*) considered analogous data on the alkaline Si–H cleavage of a series of alkyl-silanes. Again the activation entropy decreased with increasing dimensions of alkyl ligands. Moreover Taft recognized a parallel between the activation entropy of the alkyl-silane hydrolysis and the absolute entropy content of the homomorphic hydrocarbon compounds related to the alkyl-silanes. This suggests that vibrations of the entire silane molecule are involved in the creation of the transition state.

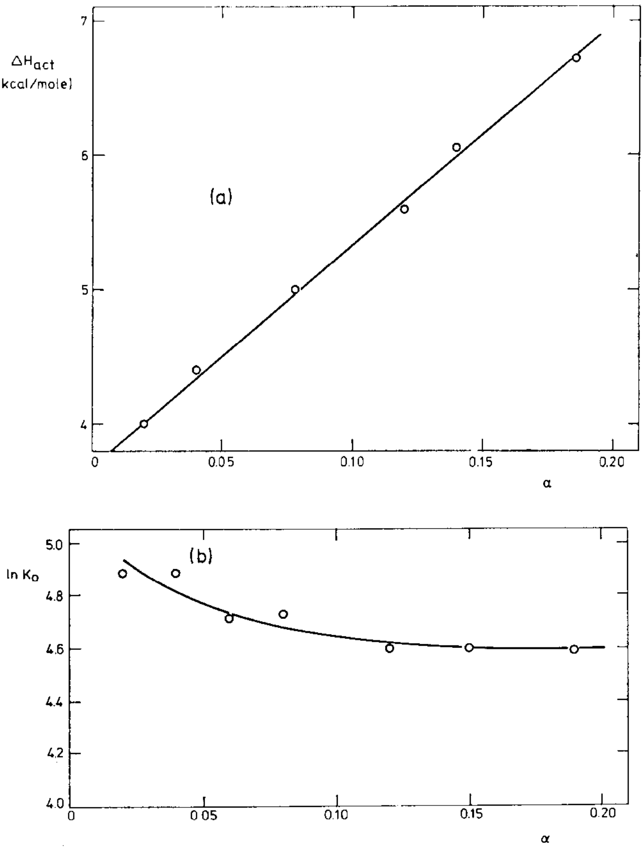

FIG. 7. Variation of activation enthalpy and entropy in the defluoridation reaction of sarin adsorbed on alumina. (a) enthalpy (b) frequency factor (k_0 in min^{-1}).

Taft mentions this effect as a "freezing" of the vibration entropy.

In the reaction in study now certainly more than one vibrational mode is involved in the rate-determining step. Even when the uptake of a hydroxyl and the departure of the fluoride are not simultaneous, the reaction is still concerted, because all ligand bonds are subject to mutual changes in bond angles, and because bond distances change in the conversion from the original tetrahedron to the trigonal bipyramid coordination of the transition state. Consequently all these bonds take part in the reaction mode and a substantial loss of vibrational entropy may result. This has an important impact upon the equilibrium between reactants and activated complex.

If loss of vibrational entropy does occur, it is interesting to know to what extent this may influence the frequency factor. Approximating the entropy of each vibration with the formula for a harmonic oscillator (*11*), one may calculate the total vibrational entropy content of an adsorbed sarin molecule from the known ir and Raman spectra (*1*a); it is about 27 e.u. at 303°K, if the two wagging vibrations of the surface-sarin bond are included (*2*b). This would apparently be a very important contribution. Summation of this limit value and the maximum loss of rotation entropy would diminish the discrepancy from a factor 10^{10} to 35.

The hypothesis on contributions from vibrational entropies implies a departure from transition state theory in that the reaction mode does not coincide with a single vibrational degree of freedom in the activated complex. Although there are experimental indications from different systems that vibrational entropy is involved in the formation of the activated complex, it is stressed that the purpose of this hypothesis is to explain only the existence but not the width of the discrepancy between the experimental frequency factor and the one predicted by transition state theory.

Origin of the Variation in Activation Energy

The origin of the distribution in activation energy may be found either in intrinsic surface inhomogeneities or in effects ultimately connected with the adsorbate (induced heterogeneity). In the former case the reaction should proceed equally fast all over the surface, showing variations on a molecular scale only, whereas the change in the adsorbed molecules causes a perturbation of the adsorbent resulting in a uniform rise in activation energy of all surface sites.

Induced heterogeneity may be precluded on the basis of experimental evidence. During the defluoridation reaction of sarin on alumina two induction effects may be recognized having identical consequences: both the adsorption of a fluoride ion on the surface and the formation of a second bonding to the surface acidify the adsorbent. The influence of the fluoride is understood from the effect caused by doping alumina with hydrogen fluoride (*16*). Lewis as well as Brønsted acid sites become stronger because of the high electronegativity of the fluoride ion. Formation of the second bonding to the surface has a similar effect. The rate-determining step of the reaction is the entering of a hydroxyl into the coordination of phosphorus. Thus two counteracting effects are expected from the increased acidity:

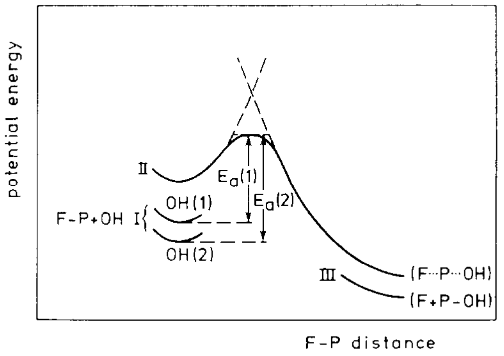

FIG. 8. A schematic picture of the potential energy contents of the reactants during defluoridation. The activation energy is indicated for two cases: hydroxyl (1) has a smaller distance to the sarin molecule than hydroxyl (2). See text for further explanation.

1. The phosphorus of an unreacted sarin molecule adsorbed on an acidified Lewis acid site becomes more positive; therefore it is more susceptible to nucleophilic attack by a hydroxyl and, consequently, the rate constant increases.
2. The surface hydroxyls become less basic and thereby less active in interacting with the phosphorus, which causes the rate constant to decrease.

If significant at all, the total induction effect of the adsorption of produced HF and of the formation of a second bonding to the surface must operate through a weakening of the basicity, because the rate constant has been observed to decrease during the reaction. However, when a sarin decomposition is performed on alumina pretreated in a hydrogen fluoride atmosphere, the range of measured reaction rate constants is not affected (*1*b, *2*b); the fastest reaction rate constant (k_1) was measured to be 0.09 min^{-1}, while on pure alumina k_1-values of 0.09 and 0.10 had been found. The number of active sites on HF-doped alumina decreased uniformly by a factor of three. Prolonged HF pretreatment accomplishes even total poisoning of the alumina (*1*a, *2*a). As the magnitudes of the rate constants are not altered, induced heterogeneity may be precluded as a cause of the variation in activation energy. So intrinsic surface inhomogeneity is responsible for the distribution in activation energy.

The rectangular shape of the distribution function suggests that only one parameter determines the activation energy. If more factors were operative, the distribution would more probably resemble a Gaussian curve.

Two parameters are to be considered as alternative explanations of the variation in activation energy. (i) The acid and basic strength of the surface hydroxyls show a scatter as is evident from the broad range of OH stretching frequencies in the ir spectrum of alumina. Influence of the basicity of hydroxyls on the defluoridation reaction appears from the poisoning effect by HF and from the effect of impregnating chromium(VI) oxide on alumina (*1*a, b). (ii) The distance between reactive hydroxyl and adsorbed sarin molecule undoubtedly influences the activation energy, as is illustrated in Fig. 8. According to a procedure described by Glasstone *et al.* (*17*) Fig. 8 represents schematically the course of the potential energy of the reactants during the defluoridation reaction, which is essentially comprised in the equation $F\text{-}P + OH \rightarrow F + P\text{-}OH$. Three stages of the reaction are discerned: (I) initial situation, (II) OH has approached sarin and (through transition state) partly displaces the F, (III) F has been removed and the final P–OH bonding has been formed.

In this picture the hydroxyl–sarin distance determines the shift from stage I to II and, consequently the activation energy. As the distance sarin–OH is determined by the Al–Al distance in the alumina surface, variation in sarin–hydroxyl distances may arise from the exposure of different crystal planes.

Insufficient data are available now to decide which property determines ultimately the variation in activation energy. It should be noted also that a correlation between variations in distance and in basicity cannot be precluded a priori.

CONCLUSION

The distribution function describing the variation in activation free energy of the sarin decomposition on alumina may be derived without a priori assumptions on the basis of two verified system properties: the reaction is first order in sarin on each set of uniform sites and the sarin molecules are adsorbed immobile. The variation in activation free energy is to be found in the activation enthalpy only, which varies from 4 to 7 kcal/mole; the frequency factor does not vary significantly.

The calculation procedure which eventually leads to the distributions in activation entropy and enthalpy may be applied to other processes as well, e.g., chemisorption.

The value of the frequency factor shows a discrepancy of a factor of 10^{10} compared to that predicted by the absolute rate theory. The cause of this discrepancy may be understood by assuming that vibration entropy of the participating reactants is lost in the transition state. This assumption implies a departure from the basic equilibrium hypothesis of the absolute rate theory.

The variation in activation enthalpy originates from intrinsic surface properties of the alumina; insufficient data are available to decide whether the distance sarin–reactive hydroxyl or the basic strength of the hydroxyls ultimately determines this variation.

ACKNOWLEDGMENT

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