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Kinetic Compensation Effects and Activated States for Alcohol Decomposition over Alkali-Modified Vanadium Oxides

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The rate of thermal decomposition of ethanol, isopropanol, and t-butanol over well-defined alkali vanadates (trivanadate, MV_3O_8, M = Li, Na, and K; and hexavanadate, $M_2V_6O_{16}$, M = Rb and Cs) were precisely measured in a closed cyclic reaction system at constant reactant vapor pressures between temperatures of 190 and 370°C. A steady rate was evident in the initial 20 min for most of the experiments. The initial mean rate decreased in the order Li → Na → K for the trivanadate. However, the initial mean rate increased in the order Rb → Cs for the hexavanadate. The plot of rate versus alkali ion size was a U-shaped curve for each alcohol run. The activation energies (E_a) for the hexavanadates were much larger than those for the trivanadates with any alcohol tested. Despite the kinetic differences between the tri- and hexavanadates, a linear relationship was found between the preexponential factor (log V_0) and the activation energy (E_a) through the series of alkali-modified vanadates for any alcohol. The data depended on the alkali ion size. The slope of the plot increased as the size of the alkyl group on the reactants increased. This compensation effect can be explained by assuming that the activation entropy is proportional to the excitation of the internal frictional rotation of an alkyl group in the reactants. In other words, the entropy term is directly related to the strength of the interaction energy, when based on a model where the alkyl and hydroxyl groups of the reactant molecule interact with the surface V=O group and the alkali metal ion, which is placed on the V–O–V interchains.

INTRODUCTION

Vanadium oxide catalysts, usually promoted by alkali sulfates, have been used for SO_2 and hydrocarbon oxidation. The promotion effects have been investigated for several reaction systems by many authors. A sequence for the catalytic activity has been reported as $Li_2SO_4 < Na_2SO_4 < K_2SO_4 < Rb_2SO_4 < Cs_2SO_4$ (*1–4*). Another sequence, Li < Na < K > Rb > Cs, has also been reported by other authors (*4, 5*). However, in such catalyst systems, the sequence is affected not only by the alkali metal properties and sulfate ions but also by the support carrier (*6*). In order to exclude the anion effects, such as sulfate, a few authors have investigated simultaneous changes in the solid state and catalytic properties upon addition of only alkali metal ions to pure V_2O_5 (*7*).

Previously, we compared the catalytic property of pure V_2O_5 (Wako Pure Chem. Co., Ltd.; guaranteed grade) to scrupulously purified V_2O_5, in which trace impurities (mainly alkali metal and iron ions) were removed by a chemical treatment (*8*). The catalytic activity for CO oxidation over purified V_2O_5 was approximately two orders of magnitude greater than that over unpurified V_2O_5. However, for the purified V_2O_5, a surface reduction occurs very easily and the activity gradually decreases during the CO oxidation. For i-propanol decomposition over $Cs_xV_2O_5$, in which x is between 0.002 and 0.664, the activity increased linearly with x ($0 < x < 0.04$) but tended to decrease sharply above a content where the $Cs_2V_6O_{16}$ compound began to be formed separately in the pure V_2O_5 phase (*9, 10*). The activity of $Cs_2V_6O_{16}$ was almost constant during the i-propanol decomposition; therefore, its surface composition and structure were assumed to be stable.

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To systematically study the relationship between surface structure and catalytic activity, the decomposition rates of ethanol, i-propanol, and t-butanol over alkali tri- and hexavanadates, which have been previously characterized by IR and X-ray analyses (*11*, *12*), were measured. The reactions followed Arrhenius' law and a compensation effect between the preexponential factor and the activation energy was found for alcohol decompositions over the series of alkali vanadates. Both values simultaneously increased with an increase in the ionic radius of alkali metal contained in the catalysts. The slope of the log V_0-versus-E_a curves increased as a function of the reactant's alkyl group size. Based on these results, a model for the interaction of an alcohol molecule with the alkali-modified surfaces was proposed. The activated state of the alcohol molecule on these surfaces is also discussed.

EXPERIMENTAL

Materials and procedures. Four grams of NH_4VO_3 (Kanto Chem. Co., Ltd.; guaranteed grade) was thoroughly mixed with M_2CO_3 (M = Li, Na, K, Rb, and Cs; Kanto Chem. Co., Ltd., guaranteed grade) in an agate mortar and then reacted in an open quartz tube (o.d. = 12 mm) at 620°C for 72 h. The reaction was then quenched in ice water, crushed, and sieved before IR, X-ray, BET surface area, and catalytic activity measurements. Alkali vanadates prepared by this method have been fully characterized by IR and X-ray analyses as trivanadates of Li and Na (MV_3O_8) and hexavanadates of Rb and Cs ($M_2V_6O_{16}$). The potassium-sample was regarded as a mixture of mainly KV_3O_8, some $K_2V_8O_{21}$, and very little $K_3V_5O_{14}$ (*11*, *12*). The reactants ethanol, i-propanol, and t-butanol (Kanto Chem. Co., Ltd.; guaranteed grade) were used as received.

TABLE 1

Surface Areas of the Alkali Vanadates

Sample	Surface area (m^2/g)
R-Li	1.7
R-Na	2.1
R-K	2.8
R-Rb	1.3
R-Cs	1.0

Measurements. Surface areas of the vanadates were determined by nitrogen gas adsorption at 77 K according to the convenient BET method proposed by Samoilov and Ryabov (*13*). The data are summarized in Table 1. The catalytic activity was determined from the total pressure change between 5 and 20 min during the initial stage with a closed cyclic system using a MD-3300 digital manometer from the Cosumo Keiki Co., Ltd. The output signal was recorded simultaneously with a Model 2543 digital printer (Yokogawa Denki Co., Ltd) and with a Model DIR-2MI electric recorder (Ookura Denki Co., Ltd.). The vessel containing the alcohol was immersed in an ice water bath during the reaction in order to keep the vapor pressure constant, at 12 mm Hg in ethanol, 8.4 mm Hg in i-propanol, or 8.3 mm Hg in t-butanol. Twenty milligrams of the catalyst was evenly distributed over the bottom of the reaction vessel (ca. 300 ml) and then heated at the required reaction temperature in air for about 1 h as a pretreatment before the main reaction. The reaction temperature was controlled within ±1°C between 190 and 370°C. The main reaction had been previously confirmed to be the dehydration of the alcohol using a gas chromatograph column containing Porapac-Q and a mass spectrometer.

RESULTS

The decomposition rates for ethanol over the alkali tri- and hexavanadates were measured at temperatures between 310 and 370°C. The total pressure increased almost linearly with time for the initial 20 min for

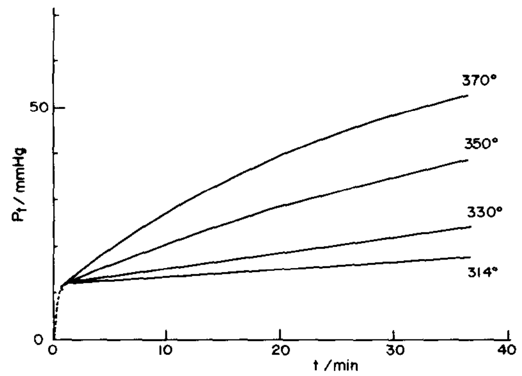

FIG. 1. Reaction curve, total pressure versus time, for ethanol decomposition over Cs-hexavanadate (R-Cs) in the temperature range 310–370°C.

all runs except in the case of the R-Cs runs at 370°C. Reaction curves for R-Cs are illustrated in Fig. 1. The pressures of these reactions increase linearly in the initial stage between 0 and 35 min at temperatures lower than 330°C. The linear relationship stops after approximately 20 min at 350°C and immediately at 370°C. Arrhenius plots for the mean rates between 5 and 20 min in the initial stage are shown in Fig. 2.

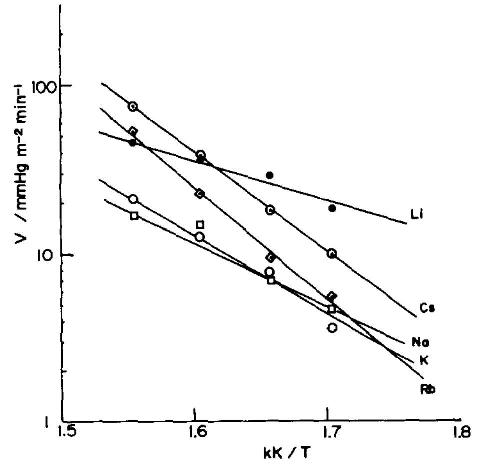

FIG. 2. Arrhenius plots for the mean rates between 5 and 20 min in the initial stage of ethanol decomposition over the alkali vanadates (R-Li to R-Cs). The rate, V, has the dimensions of total pressure change per square meter and per minute under ca. 500 ml of reaction volume; liters · mm Hg/0.5 m^2 · min.

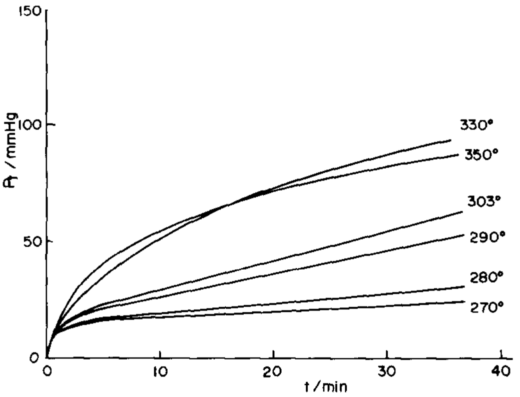

FIG. 3. Reaction curve for i-propanol decomposition over R-Cs in the temperature range 270–330°C.

The decomposition rates for i-propanol over the vanadates were measured at temperatures between 270 and 330°C. On R-Li, R-Na, and R-K, steady rates were obtained for the initial 35 min at all temperatures. However, in the cases of R-Rb and R-Cs, especially at temperatures higher than 330°C, no steady rate was observed. The reaction curves on R-Cs are illustrated in Fig. 3, in which the steady rates are seen

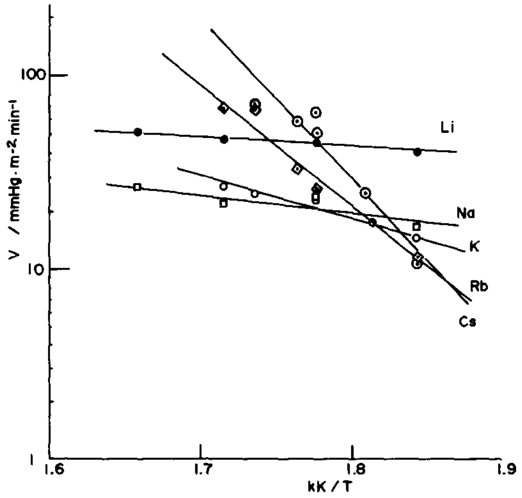

FIG. 4. Arrhenius plots for the mean rates between 5 and 20 min in the initial stage of i-propanol decomposition over the alkali vanadates (R-Li to R-Cs). The unit of the rate, V, is liters · mm Hg/0.5 m^2 · min.

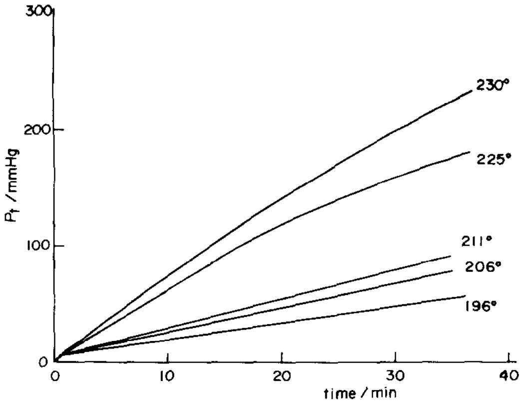

FIG. 5. Reaction curve for t-butanol decomposition over R-Cs in the temperature range 190–250°C.

only at temperatures lower than 303°C. Arrhenius plots for the initial mean rates between 5 and 20 min are shown in Fig. 4. On R-Cs, the data at temperatures higher than 303°C deviate from a linear relationship. On R-Rb and R-K they deviate at 330°C.

The decomposition rates for t-butanol over the vanadates were measured in the temperature range between 190 and 250°C. Steady rates were obtained in almost all the experiments. Reaction curves for the R-Cs are illustrated in Fig. 5. Arrhenius plots for the initial mean rates between 5 and 20 min are shown in Fig. 6. Good linear relationships are obtained in all experiments except those on R-Cs at 250°C.

Figures 2, 4, and 6, generally show that with a larger ionic radius of the alkali metal incorporated into the vanadates, the slope of the Arrhenius plots, i.e., the activation energy, tends to become larger. Especially for the i-propanol and t-butanol decompositions, the activation energies on the trivanadates (R-Li, R-Na, and R-K) are much smaller than those on the hexavanadates (R-Rb and R-Cs). Both the preexponential factor (log V_0) and the activation energy (E_a) were estimated from those Arrhenius plots and are summarized in Table 2. For any alcohol experiment the plots of log V_0 versus E_a were linear as shown in Fig. 7. Furthermore, both log V_0 and E_a tend to increase simultaneously in the following sequence; Li → N → K → Rb → Cs-vanadate. It is especially noted in Fig. 7 that the larger the slope of the log V_0–E_a curve, the larger the alkyl group of the reactants.

Ionic radii of alkali metal ions are summarized in Table 3.

TABLE 2

Arrhenius Parameters for the Alcohol Decompositions over the Alkali Vanadates, R-Li to R-Cs[a]

Sample	Ethanol		i-Propanol		t-Butanol	
	Log V_0	E_a	Log V_0	E_a	Log V_0	E_a
R-Li	5.2	10	2.4	1.6	3.1	2.6
R-Na	7.1	17	2.9	3.7	2.9	2.1
R-K	8.8	22	6.0	12	3.9	4.5
R-Rb	12	30	13	29	11	20
R-Cs	11	27	17	38	13	24

[a] Log V_0 values in liters · mm Hg/0.5 m^2 min; E_a in kcal/mol.

DISCUSSION

Kinetic Feature and Surface Structure

The type of V–O–V linkage in the alkali trivanadate differs significantly from that in the alkali hexavanadate. In Li-trivanadate,

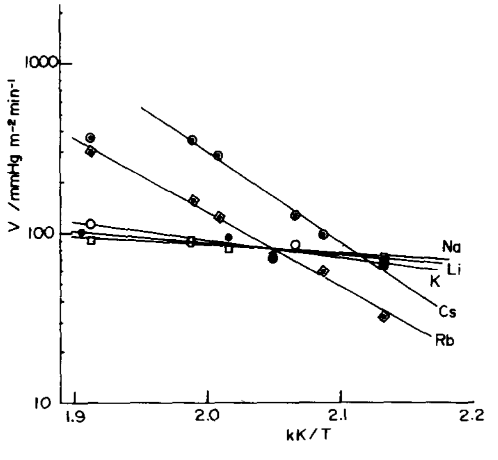

FIG. 6. Arrhenius plots for the mean rates between 5 and 20 min in the initial stage of t-butanol decomposition over the alkali vanadates (R-Li to R-Cs). The unit of the rate, V, is liters · mm Hg/0.5 m^2 · min.

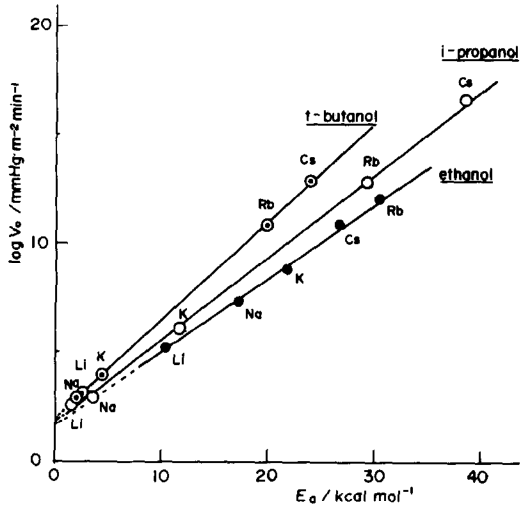

FIG. 7. Relationship between the preexponential factor (log V_0) and the activation energy (E_a) for ethanol, i-propanol, and t-butanol decomposition over the alkali vanadates (R-Li to R-Cs).

the V_3O_8 group has been confirmed to be a fundamental unit (*14*) in the linkage while in Cs-hexavanadate it is the V_2O_8 group (*15*). The *d* value for the (100) plane expands in the order Li (6.36 Å) → Na (7.0 Å) → K (8.2 Å) trivanadate (*12, 14*) and in the order Rb (7.58 Å) → Cs (8.21 Å) hexavanadate (*11, 16*).

In any of the alcohol experiments, the mean rates tend to decrease with increasing ion size of the alkali metal on the trivanadate (Li → Na → K-trivanadate). On the other hand, the mean rates tend to increase with increasing ion size on the hexavanadate (Rb → Cs-hexavanadate). The plots of the mean rates versus the alkali ion size (*17*) in the catalysts give a U-shaped curve for each alcohol experiment, as shown in Figs. 8–10. Furthermore, the activation energy (E_a) on the trivanadate was much smaller than that on the hexavanadate, especially in the case of i-propanol and t-butanol decompositions, as has been previously mentioned (cf. Figs. 4 and 6). These results clearly suggest that their kinetic properties are very closely related to the type of V–O–V linkage in the catalysts. Thus, these catalytic systems might be classified as structurally sensitive (*18*). The U-shaped activity curve, where the activity becomes a minimum for the K-vanadates, has not been previously reported (*1–4*). This activity curve is opposite that reported by Fikis *et al.* (*5*) and Vol'fson *et al.* (*6*). We do not fully understand the implications of these data, but the inconsistencies might arise from the difference in alkali metal content

TABLE 3

Ionic Radii of Alkali Metal Ions, M^+ (*17*)

Alkali metal	Ionic radius (Å)
Li	0.68
Na	0.97
K	1.33
Rb	1.52
Cs	1.70

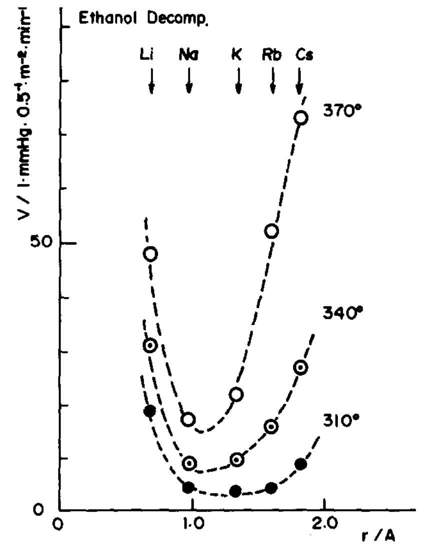

FIG. 8. Plots of the initial mean rates (5–20 min) for ethanol decomposition versus the ion size of alkali metal incorporated into the vanadates. The rates at the three temperature were estimated from the Arrhenius plots in Fig. 2.

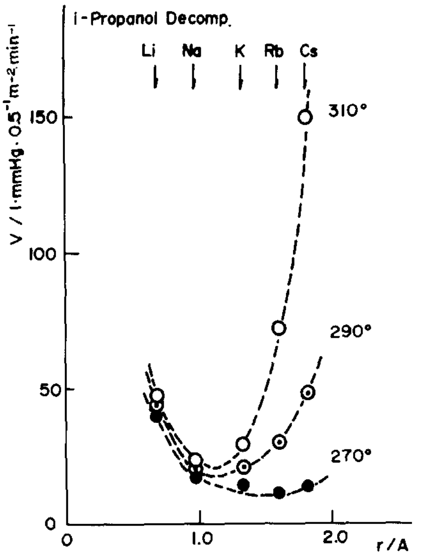

FIG. 9. Plots of the initial mean rates (5–20 min) for i-propanol decomposition versus the ionic radius of alkali metal. The rates at the three temperatures were estimated from the Arrhenius plots in Fig. 4.

which will cause differences in the surface structure.

Compensation Effect and Activated State

The good linear relationship between the preexponential factors and the activation energies for any of the alcohol decompositions on the series of alkali-modified vanadates, without respect to the difference in structure between tri- and hexavanadates, are shown in Fig. 7. This means that a relatively large E_a, determined for the hexavanadate, is compensated by a correspondingly large activated entropy term, while a small E_a, for the trivanadate, is compensated by a small entropy term.

A linear relationship between the Arrhenius parameters, log k_0 and E_a, has generally been found for various homogeneous and heterogeneous reaction systems. It is called a "compensation effect." The compensation effect has been interpreted and reviewed in several articles (*19*) and monographs (*20*). Recently, an explanation for this effect was also put forward by several authors (*21–23*). For instance, Conners (*21*) tried to explain, in general, the compensation effects based on a statistical treatment of the vibrational (as a harmonic oscillator) and rotational modes of the activated species. McCoy (*23*) has proposed a quantum mechanical model to explain the large reaction rate increase of the catalyzed dissociation steps based on the effect of the anharmonic nature of the oscillating bound species and interaction with the catalyst. He introduced an Arrhenius-type equation that is very sensitive to the value of the anharmonicity parameter and pointed out that the equation showed a compensation effect similar to that observed with numerous catalytic reactions. Cremer explained the kinetic compensation effect in terms of an activated entropy term which could only be caused by the excitation of vibrational quanta of an activated species. In this discussion, however, we assume that the entropy term is proportional to the excitation of the inner frictional rotation of the alkyl

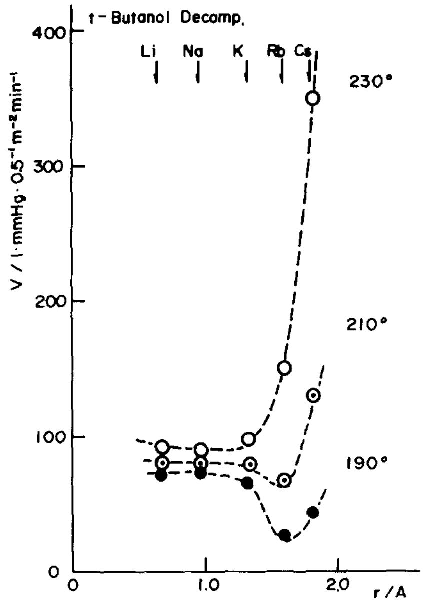

FIG. 10. Plots of the initial mean rates (5–20 min) for t-butanol decomposition versus the ionic radius of alkali metal. The rates at the three temperatures were estiamted from the Arrhenius plots in Fig. 6.

groups in the activated alcohol molecule. In fact, the frictional rotation states of the alkyl group can be expected to be controlled mainly by the initial adsorbed states, R_1 and R_2 in Figure A1, as reported by Cremer (*19a*). Furthermore, the frictional rotation, restricted in the adsorbed state, may be allowed to some extent in the activated states, $A_1^\ddagger$ and $A_2^\ddagger$ of Fig. A1. In a large alcohol molecule such as t-butanol, the contribution of the internal frictional rotation of not only the t-butyl group but also the three methyl groups to the entropy term cannot be negated in the activated state.

The entropies caused by the frictional rotation of alkyl groups have been calculated by Benson (*24*). The values, divided by the gas constant, S_f^0(int.)/R, are listed in the second column of Table 4. According to the above description, the activated entropy term (log V_0) is directly proportional to the total entropy, which has been estimated from the frictional rotation of the alkyl group of an alcohol molecule and all methyl groups contained in the group, as listed in the third column of Table 4. The relative change in the entropy (Δ log V_0) with alkali modification of the surface can be expected to be proportional to the S_f^0(int.total)/R value for the related alcohol. On the other hand, according to the linear free energy relationship (LFER: Horiuchi–Polani rule) (*25*), the activation energy for the dehydration reaction of an alcohol is directly proportional to the bonding energy of R-OH, E(R-OH), for each alcohol. These values are given in the second column of Table 5.

TABLE 4

Evaluation of Entropies of Alkali Groups as Internal Frictional Rotators at 600 K (*24*)

Group	S_f^0(int.)/R	S_f^0(int. total)/R
Methyl	3.27	3.27
Ethyl	4.12	4.12 + 3.27 = 7.4
i-Propyl	4.68	4.68 + 2 × 3.27 = 11.2
t-Butyl	4.78	4.78 + 3 × 3.27 = 14.6

TABLE 5

Bonding Energies of R–OH in Alcohol Molecules, Ratios of S_f^0(int. total)/R to E(R–OH), and Δ Log $V_0/\Delta E_a$ Estimated from the Curves in Fig. 7

Alcohol	E(R–OH) (kJ/mol)	S_f^0(int. total)/R · E(R–OH) (kJ/mol)$^{-1}$	Δ log $V_0/\Delta E_a$ (kJ/mol)$^{-1}$
Ethanol	383	0.0193	0.350
i-Propanol	385	0.0291	0.405
t-Butanol	379	0.0385	0.465

Furthermore, the relative change in the activation energy (ΔE_a) with alkali modification can also be expected to be proportional to the E(R-OH) value for the related alcohol. Therefore, the ratio, S_f^0(int. total)/R · E(R-OH), given in the third column of Table 5, is theorized to correlate to the activated entropy change divided by the activation energy change, Δ log $V_0/\Delta E_a$, which are given in the fourth column of Table 5. The plot of Δ log $V_0/\Delta E_a$ versus S_f^0(int. total)/R · E(R-OH) for each alcohol had a good linear relationship, as shown in Fig. 11. The present compensation effect was confirmed by the excitation term of the rotational quanta instead of the vibrational quanta in the activated state. At present we do not know about the vibrational excitation modes of any adsorbed species (as a harmonic or anharmonic oscillator) in the activated state. Therefore, we use the present procedure for analyzing the kinetic parameters in order to find an effective catalytic system.

Gentry *et al.* (*26*) proposed a surface interaction model where the hydroxyl group of an alcohol molecule interacts with a surface positive site. Based on such an interaction model for the hydroxyl group of an alcohol molecule directly interacting with the alkali metal ion incorporated into the V–O–V interlayers, we can postulate that the interaction energy becomes smaller in the order R-Li → Na → K → Rb → Cs because the ionic radius of the alkali metal increases with a corresponding decrease in the polar-

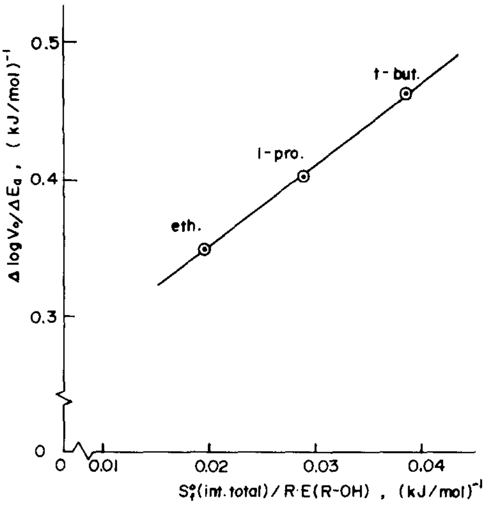

FIG. 11. The correlation between the values of Δ log $V_0/\Delta E_a$ and the S_f^0(int. total)/R · E(R-OH), which are summarized in Table 5. The former was estimated empirically from Fig. 7 and the latter from the entropy (S_f^0) caused by the internal frictional rotation of the alkyl group and the bonding energy of R-OH. E(R-OH). See text for more detail.

izability. Furthermore, the shorter the d value for the (100) plane, the closer the alkali group can come to the surface V=O group and the lower will be the activation enthalpy and entropy. This theory fits the compensation relationship shown in Fig. 7. Although the activity of the alkali trivanadate differed considerably from that of the hexavanadate, the kinetic compensation effect held completely for the reaction systems. Therefore, a compensation effect will usually be found for a series of reaction systems similar in the activated state, even if the structural aspect of the catalyst surface differs from the tri- or hexavanadates.

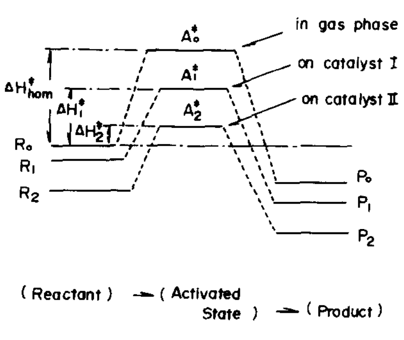

FIG. A1. Energy diagram for an elemental reaction step. Changes in energy levels under the existence of Catalysts I and II, which act strongly and weakly, respectively (*19a*).

APPENDIX

An energy diagram for an elemental reaction step was determined by Cremer and is shown in Fig. A1 [cf. Fig. 4 in Ref. (*19a*)]. When an elemental reaction occurs noncatalytically from R_0 to P_0 by way of an activated state, $A_0^\ddagger$, the rate constant is expressed, according to Eyring and co-workers (*27*), by

$$k_0 = (kT/h)\exp(\Delta S_0^\ddagger/R)\exp(\Delta H_0^\ddagger/RT) \quad \text{(A1)}$$

$$\log k_0 = (\log(kT/h) + \Delta S_0^\ddagger/2.302R) - \Delta H_0^\ddagger/2.302RT. \quad \text{(A2)}$$

The energy level of the activated state, $A_0^\ddagger$, becomes $A_1^\ddagger$ in the presence of catalyst I. With catalyst II, which interacts with the reactant more strongly than catalyst I, the activated state, $A_2^\ddagger$, is placed on a level much lower than $A_1^\ddagger$; that is, $A_0^\ddagger > A_1^\ddagger > A_2^\ddagger$. Therefore, the activation enthalpy with catalyst I, $\Delta H_1^\ddagger$, determined from Fig. A1, is larger than that using catalyst II, $\Delta H_2^\ddagger$. The vibrational quanta for the bond formed between the activated complex and the catalyst surface may be excited more easily on catalyst I as compared to catalyst II, i.e., $S_1^\ddagger > S_2^\ddagger$. This suggests that the relationship $\Delta S_1^\ddagger > \Delta S_2^\ddagger$ is correct. Therefore, $\Delta H_1^\ddagger > \Delta H_2^\ddagger$ corresponds to $\Delta S_1^\ddagger > \Delta S_2^\ddagger$, and shows the existence of the compensation effect.

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