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Heats of Polymerizaton of 1-Butene over Silica-Alumina

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The surface reaction between 1-butene and silica-alumina at 30°C has been examined by calorimetric techniques. Equations have been developed for calculating the heat involved in the surface reaction. Heats of 8–10 kcal/mole were observed initially, increasing to 15–16 kcal/mole with increasing pressure of 1-butene. The heats are indicative of the polymeric nature of the product of the surface reaction. Dimers are formed initially at low pressure and the average degree of polymerization increases with increasing pressure.

INTRODUCTION

Calorimetric techniques have been used extensively to determine differential heats of adsorption of gases on solid surfaces (*1–6*). It is well-known that these heats decrease with increasing coverage of the solid surface as sites of lower energy are covered. Simultaneous determination of heats of adsorption and adsorption isotherms have allowed estimates of the site-energy distribution on solid surfaces to be made. We have been particularly interested in the nature of the sites active in the isomerization and polymerization of 1-butene over silica-alumina. In a recent paper, Clark and Finch (7) have shown that 1-butene is rapidly adsorbed on silica-alumina at 25°C and an irreversibly adsorbed polymeric complex is formed. Ammonia blocking techniques have shown that this complex is associated in some manner with activity for the isomerization reaction. The amount of polymeric complex increased with increasing partial pressure of 1-butene and, assuming that one ammonia molecule occupied one active site, calculation showed that the average degree of polymerization varied from dimer to pentamer for pressures ranging 8–50 mm. In the present work we have followed the formation of this polymeric complex calorimetrically to obtain additional information on the degree of polymerization and to extend the application of calorimetric data beyond the determination of heats of adsorption to the study of surface reactions.

EXPERIMENTAL

The thermocouple vacuum calorimeter used in this work is shown in Fig. 1 and is similar to those described by Beebe (*8*) and Garner and Veal (*9*). The calorimeter cell was constructed of quartz and was 28 cm overall length and 21 mm i.d. at the widest point. The inner wall of the vacuum jacket was platinized to reduce radiation losses and the cell was attached to the gas handling system by Viton A O-ring joints. Two 36-gauge chromel-alumel thermocouples were introduced through Kovar seals in the upper Pyrex section using 40–60 lead-tin solder to obtain gas-tight seals. The internal wires were insulated with glass sleeving. The catalyst was held in a porous silica bucket suspended from the thermocouples. This bucket was formed from $^3\!/_8$-in Refrasil sleeving by placing it over a carbon mandrel and flaming with an oxy-hydrogen torch to close one end and form stiffening ribs. The bucket was held just above the midpoint of the catalyst bed and only one thermocouple was used during a measurement. The heat capacity of the calorimeter was calculated from handbook values for silica and alumina and the known weights of each in the system. The volume of the section shown in Fig. 1 was 76 cm^3 and combined with the 87 cm^3 volume of the gas handling manifold gave a total volume of 163 cm^3.

A conventional gas handling and storage system was used. A vacuum of 10^{-5} mm was obtained with a mercury diffusion pump and mechanical forepump. Pressures were measured using a Texas Instruments Model 141 bourdon type gauge with servo-nulling and automatic readout. The accuracy of the gauge was ±0.015 mm.

The thermal emf was measured on a Keithley Instruments Model 147 nanovolt null detector using a Keithley Instruments Model 260 nanovolt source to level part of the emf. The cold junctions of the thermocouples were kept in an ice bath.

The catalyst was a sample of Houdry M-46 silica-alumina containing 87% SiO_2 and 13% Al_2O_3 from the same batch used in the previous work (7). The BET surface area was 300 m^2/g. The 30–100 mesh catalyst was activated at 500°C for 16 hr in a stream of dry air in a separate apparatus. It was allowed to cool and 0.75 g loaded into the catalyst bucket of the calorimeter. Then the catalyst was given an additional heat treatment at 500°C for 2 hr under vacuum. After cooling to room temperature under vacuum, the calorimeter was surrounded by a well-insulated furnace containing an aluminum block 17.8 cm in diameter and 30.5 cm high drilled out to accommodate the cell. The block was heated by resistance elements and maintained at 30° ±0.01°C by a thermatrol temperature controller. All experiments were done at this temperature.

Phillips Research Grade 1-butene was used as received as were the ammonia and

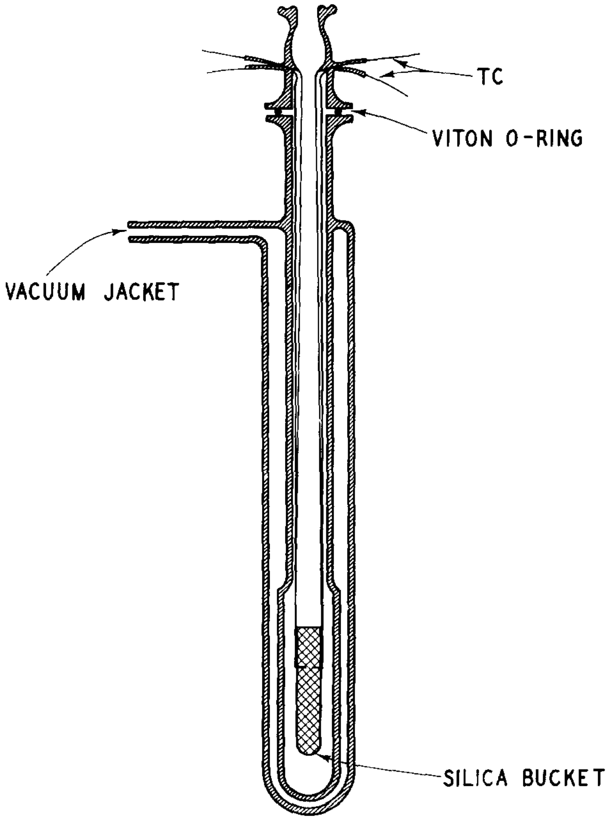

Fig. 1. Thermocouple vacuum calorimeter.

ultrahigh purity argon obtained from Matheson Company.

Single junction thermocouple vacuum calorimeters of the type used here are subject to errors from thermal gradients and nonselective adsorption effects as has been pointed out by Garner and Veal (*9*). We have used the porous bucket to reduce nonselective adsorption effects and thermal gradients were minimized by introducing 0.2 mm of argon into the cell before the first increment of 1-butene was admitted. The calorimeter did not have an internal resistance element for absolute calibration. Therefore, we have chosen the adsorption of *n*-butane on carbon black (graphon) as a test of the calorimeter because of the uniformity of the graphon surface and the availability of literature values for the heat of adsorption. We have obtained values for the initial heat of adsorption of 10.1 kcal/mole which compares well with the results of Beebe, *et al.* (*10*) who obtained a value of 10 kcal/mole. Kiselev (*11*) has given an average heat at 50% coverage of 8–8.5 kcal/mole and we have obtained a value of 7.5 kcal/mole. We believe that these results demonstrate the accuracy and reliability of the calorimeter.

METHODS OF CALCULATION

Gravelle and Teichner (*12*) have studied surface reactions occurring during the oxidation of carbon monoxide on nickel oxide and have shown that the profiles of the calorimetric cooling curves were irregular when more than one process was occurring. We have found irregularities in the calorimetric cooling curves obtained when 1-butene is adsorbed on silica-alumina. These irregularities are in the form of deviations from Newton's law of cooling. Three typical experimental cooling curves are shown in Fig. 2. The curve for ammonia adsorption on silica-alumina represents the case of rapid evolution of heat due to adsorption followed by Newtonian cooling. In the case of 1-butene, the rate of cooling is considerably less and non-Newtonian indicating that heat is being supplied after any initial adsorption has ceased. The cooling curve obtained for 1-butene adsorption on ammonia poisoned silica-alumina is Newtonian. There is no heat supplied after the initial adsorption and the rate of cooling in the presence of 1-butene is the same as that found in the presence of ammonia. The heats responsible for non-Newtonian behavior were calculated from a heat balance on the calorimetric cooling curves in the following manner, representing a modification of the method of Tian (*13*).

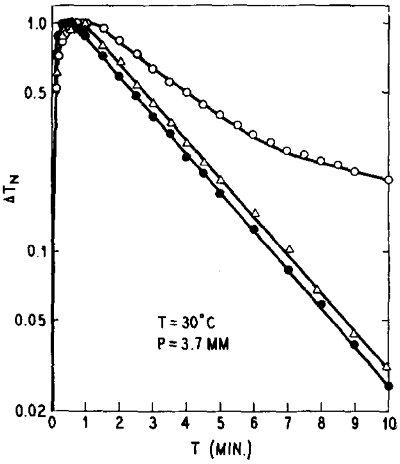

FIG. 2. Experimental cooling curves for ammonia (●) and 1-butene (○) over silica-alumina and 1-butene (△) over ammonia poisoned silica-alumina ($\Delta T_N \equiv$ normalized temperature change).

At any point on the cooling curve after the initial heat of adsorption, the rate of change of temperature in the calorimeter, dT/dt, may be expressed as the sum of the instantaneous rate of cooling, $(dT/dt)c$, and the instantaneous rate of heating due to polymerization, $(dT/dt)p$.

$$\frac{dT}{dt} = \left(\frac{dT}{dt}\right)_c + \left(\frac{dT}{dt}\right)_p. \qquad (1)$$

The cooling rate is expressed by Newton's law,

$$\left(\frac{dT}{dt}\right)_c = -\alpha(T - T_0), \qquad (2)$$

where α is the cooling coefficient and T_0 the baseline temperature before any heat release. The rate of heating due to polymerization may be expressed by

$$\left(\frac{dT}{dt}\right)_p = \frac{VQ_p}{C_c}\frac{dN_v}{dt}, \tag{3}$$

where N_v is the number of moles of monomer per unit volume, V is the volume of the calorimeter, Q_p is the heat of polymerization per mole of monomer and C_c is the heat capacity of the system. The reaction rate, dN_v/dt may be rewritten as,

$$\frac{dN_v}{dt} = -\frac{1}{RT_0}kP^n(t), \tag{4}$$

where k is the rate constant and n, the order of the reaction. Substituting Eq. (4) into Eq. (3), we may write the net rate of temperature change:

$$\frac{dT}{dt} = -\alpha(T - T_0) - \beta P^n(t), \quad \beta = \frac{VkQ_p}{RT_0C_c}. \tag{5}$$

The polymerization reaction was found to be first order so that we may write,

$$P(t) = P_0e^{-kt} \tag{6}$$

and

$$\frac{dT}{dt} = -\alpha(T - T_0) - \beta P_0e^{-kt}. \tag{7}$$

Integrating Eq. (7) and rearranging, we obtain

$$\beta = \frac{[(T_{\max} - T_0) - (T - T_0)(e^{\alpha t})](\alpha - k)}{P_0[e(\alpha - k)t - 1]}, \tag{8}$$

where $T_{\max} = T$ at $t = 0$. Typical values of $T_{\max}$—T_0 were in the range 0.75–1.0°C. Values of T and t are taken from the experimental calorimetric curve and since all other terms are known, β is calculated. And from known values of β, Q_p may be calculated from

$$Q_p = \frac{RT_0C_c\beta}{Vk}. \tag{9}$$

RESULTS AND DISCUSSION

In order to solve Eq. (8) for β, the cooling coefficient, α, must be known over the range of pressure used in determining the heat of polymerization. We have used the adsorption of ammonia on silica-alumina for this purpose since the only heat involved is that of rapid adsorption as shown by Stone and Whalley (*14*). No secondary processes are involved which would alter the cooling coefficient as the pressure of ammonia is increased. The cooling coefficient was determined from the slope of plots of ln (T — T_0) vs t over the pressure range 0.2 mm–19.2 mm. The pressures, P_f, referred to are the pressures at the termination of each incremental addition of ammonia. It was found that α increased with increasing pressure in the calorimeter. This is the result of improved thermal conductivity between grains and the reduced effect of nonselective adsorption as pressure increases. A plot of α vs P_f is shown in Fig. 3. Initially α had a value of 0.23 min^{-1} at 0.2 mm and increased rapidly to a value of 0.41 min^{-1} at 3.5 mm after which it remained constant up to 19.2 mm, the highest pressure used.

When small increments of 1-butene (0.2 cm^3 STP) were admitted to the calorimeter containing silica-alumina, there was an initial rapid uptake of 1-butene followed by a much slower uptake. Initially, Newton's cooling law was obeyed. During the slow uptake, however, deviations from Newton's cooling law were found. This deviation is caused by the additional heat of polymerization supplied to the system

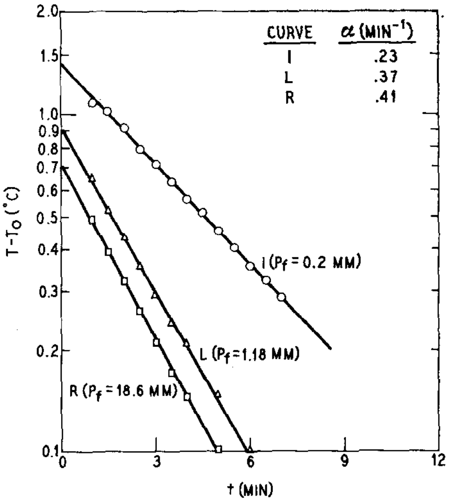

FIG. 3. Variation of cooling coefficient (α) with pressure (P_f).

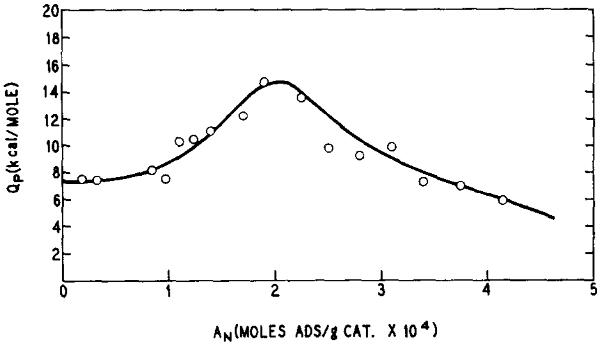

FIG. 4. Heat of polymerization of 1-butene over silica-alumina (I) at 30°C.

during the slow uptake of 1-butene after the initial rapid evolution of the heat of adsorption.

The magnitude of Q_p, the heat of polymerization, which causes deviation from Newtonian cooling was calculated using Eqs. (8) and (9) and the known values of T_0, C_c, V and α. The rate constant k was calculated from the first order Eq. (6). P_0 was obtained by extrapolation of the 1-butene uptake data back to $t = 0$. ($T_{\max} - T_0$) was obtained by extrapolation of the initial linear part of plots of ln $(T - T_0)$ vs t to $t = 0$. Knowing β and k, Q_p, the heat evolved after the initial heat of adsorption, was calculated. This procedure was repeated for each cooling curve and the results for two samples of silica-alumina are shown in Figs. 4 and 5. Typical values of k, β and Q_p are shown in Table 1.

In the initial increments, the heat evolved is in the range 8–10 kcal/mole. Subsequent increments show the increase in this heat to 15–16 kcal/mole at a coverage of 2–3 × 10^{-4} mole ads/g-catalyst. At higher coverages, the heats decline and are near 6 kcal/mole at 4 × 10^{-4} mole ads/g-catalyst.

The magnitude of the heats expected for the polymerization of 1-butene and their variation with the degree of polymerization, d, can be found from the following equation:

$$C_4H_8 \rightarrow \frac{1}{d}(C_4H_8)_d,$$

$$\Delta H_d = \frac{d-1}{d}(\Delta H_\infty).$$

ΔH_∞ for high polymers is taken as 20.7 kcal/mole (*15*). Values of ΔH_d for various values of degree of polymerization are given in Table 2.

The initial heats in the range 8–10 kcal/mole are indicative of the formation of dimers at these low pressures. The increase in the degree of polymerization from dimer to tetramer as indicated by an in-

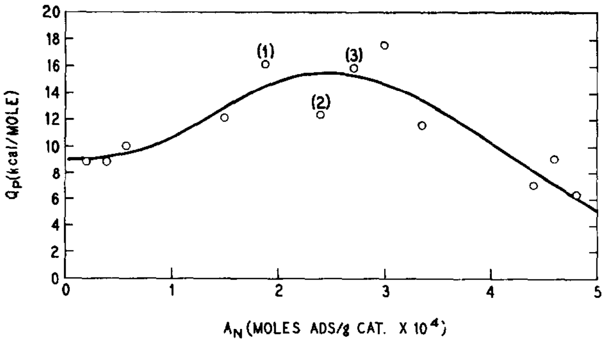

FIG. 5. Heat of polymerization of 1-butene over silica-alumina (II) at 30°C.

TABLE 1

VALUES OF k, β, AND Q_p FOR 1-BUTENE POLYMERIZATION OVER SILICA-ALUMINA (II)[a]

Cooling[b] curve	ΔP (mm)	mole ads g-catalyst $\times 10^4$	t(min)	k(min^{-1}) $\times 10^3$	β $\left(\frac{\text{deg-mole}}{\text{mm-min}}\right) \times 10^3$	Q_p $\left(\frac{\text{kcal}}{\text{mole monomer}}\right)$	Q_p (av)
1	2.43	0.35	6	19.5	14.2	15.0	
			8	17.3	13.7	16.3	16.2
			10	16.1	13.2	16.8	
			12	15.0	12.3	16.8	
2	3.54	0.51	6	20.1	11.2	11.5	
			8	17.0	11.2	13.6	12.4
			10	15.0	9.2	12.6	
			12	13.0	7.7	12.0	
3	2.92	0.42	6	10.0	7.9	16.5	
			8	8.6	6.3	15.1	15.9
			10	7.4	5.7	16.0	
			12	6.7	5.2	16.0	

[a] Weight catalyst = 0.60 g.

[b] See Fig. 5.

crease in the heat of polymerization to 15–16 kcal/mole could be due to the increasing pressure in the calorimeter and is in agreement with the work of Clark and Finch (7).

Further evidence that these heats are due to the formation of a polymeric complex of 1-butene was obtained by observing the heats evolved when 1-butene was admitted to a catalyst which had been previously saturated with ammonia at 200°C. This treatment has been shown to prevent the formation of the polymeric complex (7). In this case, the slow uptake of 1-butene was not found and the related cooling curves exhibited Newtonian behavior. The calculated heats are shown in Fig. 6 for two separate runs. The heats are low or absent except in the one case where desired saturation with ammonia at 200°C was probably not quite achieved.

TABLE 2

VARIATION OF HEAT OF POLYMERIZATION OF 1-BUTENE WITH DEGREE OF POLYMERIZATION (d)

d	ΔH_d(kcal/mole)
2	10.3
3	13.8
4	15.5
5	16.6
∞	20.7

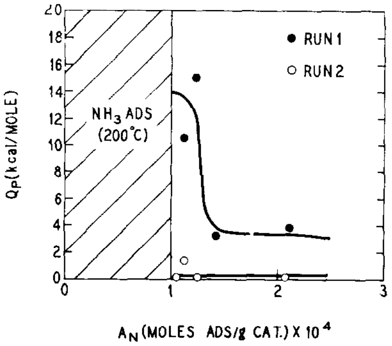

FIG. 6. Heat of polymerization of 1-butene over ammonia poisoned silica-alumina at 30°C.

The fall in heats of polymerization with further increases in pressure as shown in Figs. 4 and 5 is due to the influence of sites of progressively lower adsorption energies or to the general depletion of polymerization sites.

The fact that we can distinguish changes in degree of polymerization suggests that polymerization does not occur over an initial strongly adsorbed layer of 1-butene. If this were the case, then the heat released, Q_p, should be uniform over the entire range of adsorption attributable to polymer formation.

The initial heat of adsorption of 1-butene is difficult to measure accurately. It does not exceed 8–10 kcal/mole. If this low heat is a measure of the adsorption-bond strength, one would not expect the polymer subsequently formed on a site to be irreversibly adsorbed as shown by Clark and Finch (*7*). However, the mode of adsorption may be pictured as follows (*16*):

$$\mathrm{C::C} \rightarrow \mathrm{:\bar{C}:C^{+}} \qquad +40\ \mathrm{kcal}, \qquad (10)$$

$$\mathrm{S^{+} + :\bar{C}:C^{+}} \rightarrow \mathrm{S:C:C^{+}} \qquad -48\ \mathrm{kcal} \qquad (11)$$

$$\mathrm{S^{+} + C::C} \rightarrow \mathrm{S:C:C^{+}} \qquad -8\ \mathrm{kcal} \qquad (12)$$

S^+ represents an adsorption site and C::C represents an olefin. The endothermic heat of the first reaction (+40 kcal/mole) was estimated by Eyring (*17*) quantum mechanically. The heat of the second reaction (—48 kcal/mole) was calculated assuming the overall observed heat of adsorption given by the third equation as —8 kcal/mole. Thus, the bond strength would be measured by the second reaction (—48 kcal/mole) which is sufficiently large to account for the observed irreversible adsorption at room temperature. Net endothermic heats of adsorption, if such occur with olefins, could be explained by a mechanism of this type. If adsorption occurred directly through the π-bond, irreversible adsorption would more likely be accompanied by a large observed heat of adsorption. In comparison with the heat of polymerization in the gas phase, the heat for the adsorbed phase will contain an additional amount for the heat of adsorption. If we take a heat of adsorption of 8 kcal/mole, as in Eq. (12), then the total heat for adsorbed tetramer will be approximately 2 kcal higher than for gas phase polymerization per mole of monomer, 17.5 instead of 15.5 kcal/mole of 1-butene.

Endothermic heats of adsorption have actually been calculated for 1-butene on alumina based on Langmuir–Hinshelwood kinetics (*18*). These heats are considered to be the result of thermal activation of sites, the number of sites and amount of adsorption increasing as the temperature is increased. The thermal activation mechanism certainly explains the endothermic nature of the calculated heat. But this calculated heat may be an artifact of the Langmuir–Hinshelwood model which tacitly assumes no change in number of sites with temperature. It is doubtful if the true nature of the net heat of adsorption endothermic or exothermic, can be determined in this way.

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