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The Catalytic Hydrogenation of Ethene on the Surface of Liquid Caesium

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The self-hydrogenation of 3 mol of C_2H_4 at 20 kN m^{-2} from 363 to 489 K on the surface of a jet of liquid caesium produces 2 mol of C_2H_6. The reaction is first order with activation energy 15.8 kJ mol^{-1}. With an equal volume of H_2, the alkene is 100% catalytically hydrogenated to C_2H_6 by a first-order process with activation energy 45.5 kJ mol^{-1}. Increasing the proportion of H_2 increases the rate of catalysis. A mechanism is suggested for each process. © 1990 Academic Press, Inc.

INTRODUCTION

Clean mobile liquid alkali metals provide very chemically reactive surfaces of which the low melting Cs (mp 301.7 K) is the most active. Some gases react, however, at sufficiently slow rates at relatively low temperatures to enable study by conventional means, and H_2 (*1*) and C_2H_4 are two such examples. The present paper shows that Cs, like K (*2*), converts two-thirds of C_2H_4 to C_2H_6. When the alkene is mixed with H_2, however, there is quantitative catalytic conversion to C_2H_6 on the metal surface and the kinetics are measured for the first time.

METHODS

The Pyrex glass version of the apparatus is described schematically in Ref. (*1*). The dynamic nature of the flowing metal as it is injected into the gas is captured by the photograph (Fig. 1). Liquid Cs (150 g, Kawecki–Berylco, 99.98%) was run into the vessel under a protective atmosphere of Ar, and the metal was circulated and injected into the gas space by a miniature electromagnetic pump (*1*).[1] The entire assembly (Fig. 2, R) was enclosed in an air-oven (O), and the Ar was replaced by known pressures of C_2H_4 (99.99%, British Petroleum) and C_2H_4 + H_2 (99.98%, Air Products) from a storage bulb (G). The total pressure was measured by a manometer (M) and was recorded continuously by the pressure transducer (P) as the gases reacted with the jet and pool of continuously regenerated clean liquid metal. The volume of the capillary frame was small compared to the reaction

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[1] Caution. The hot, dense (1.8 × 10^3 kg m^{-3}), golden-coloured, metallic Cs burns vigorously in air and CO_2, emitting caustic fumes, and burns explosively with water at all temperatures. The solid (mp 301.7 K) reacts with air and becomes a mobile dark-coloured liquid (mp 253 K) due to dissolution of caesium oxides (20 mol% O). The burning molten metal can be dyked and covered with metal-fire extinguishing powder but explosions can occur with halogenated hydrocarbons. The solid metal can be protected from air by oil and disposed of by dissolution in heavy alcohols under Ar/N_2 or in liquid NH_3 (bp 240 K). The molten metal can be contained in Pyrex glass up to 523 K but darkening and embrittlement of the glass occurs at higher temperatures due to reduction of SiO_2 and the formation of caesium silicates.

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volume in R. The loss of C_2H_4 was determined at selected times by withdrawing the gases from the reaction vessel into the cell (C) and analysing by calibrated infrared spectroscopy the intensity of the C–H out-of-plane deformation absorption at 950 cm^{-1}. Gas which was noncondensable at 75 K and which was not infrared-active was assumed to be H_2, and the reaction product, C_2H_6 (identified by infrared spectroscopy), made up the remainder of the gas mixture.

RESULTS AND DISCUSSION

The Self-Hydrogenation of C_2H_4

The reaction of C_2H_4 alone with Cs was studied to aid the interpretation of the reactions of the mixtures. From 363 to 489 K and with starting pressures of C_2H_4 near 20 kN m^{-2}, the total pressure fell smoothly with time as C_2H_4 was self-hydrogenated to C_2H_6 over a period of about an hour (Fig. 3). In every case the gaseous product was solely C_2H_6 and invariably 3 mol of C_2H_4 were converted to 2 mol of C_2H_6 (Table 1). The missing carbon was assumed to be in Cs_2C_2 but the solid product was not identified directly. Generally hydrolysis of resi-

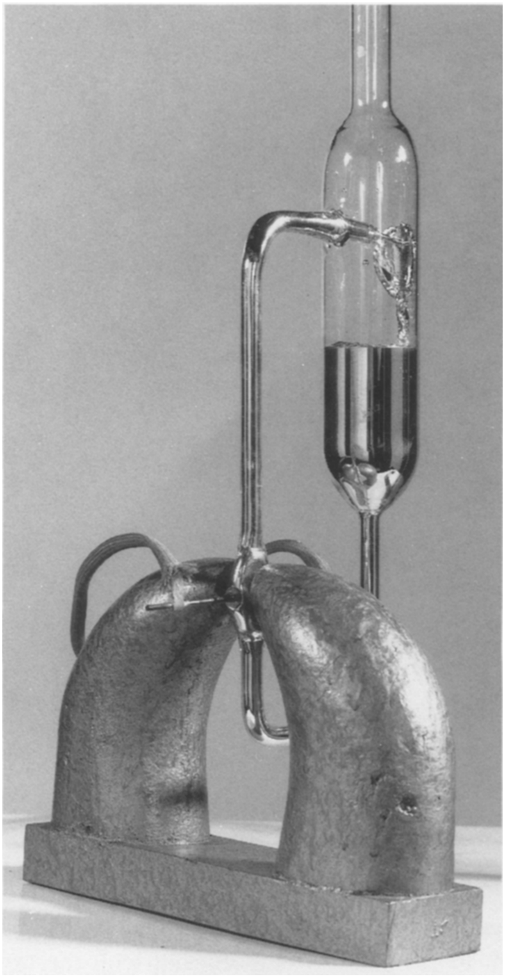

FIG. 1. Reaction vessel showing flowing liquid caesium.

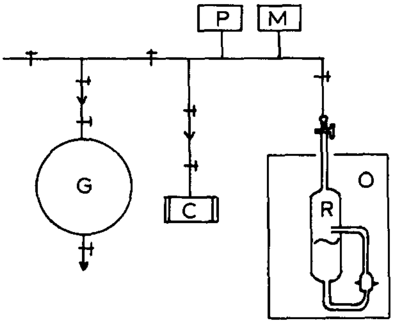

FIG. 2. Apparatus assembly.

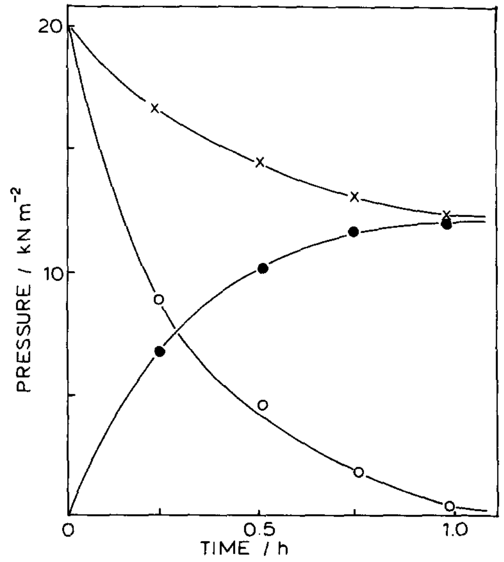

FIG. 3. Reaction of C_2H_4 on liquid Cs. (x) Total pressure, (O) pressure of C_2H_4, (●) pressure of C_2H_6.

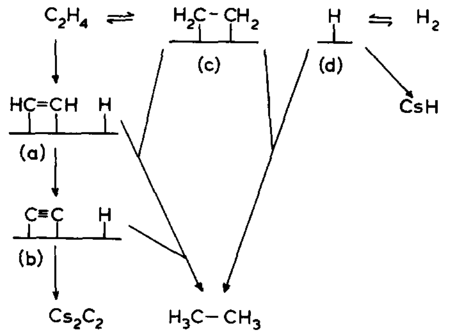

FIG. 4. Mechanisms of self-hydrogenation and catalytic hydrogenation of C_2H_4 on liquid Cs.

dues gave C_2H_2, which is indicative of Cs_2C_2, so that the reaction stoichiometry is represented by

$$3C_2H_4 + 2Cs \rightarrow 2C_2H_6 + Cs_2C_2. \quad (1)$$

The key feature is the hydrogen transfer between C_2H_4 molecules; some lost H to become ultimately C_2^{2-} whereas others gained to become C_2H_6. This suggests that two types of adsorption are involved. Some of the incoming C_2H_4 molecules were dissociatively adsorbed (Figs. 4a and 4b) to provide labile H (or adsorbed H atoms) whereas other incoming C_2H_4 molecules were associatively adsorbed (Fig. 4c) and thus able to consume the active (or adsorbed) H atoms. The constancy and preciseness of the 3 : 2 stoichiometry suggest that the associative adsorption is reversible but that the dissociative adsorption is not, and that a slow rate of formation of the dissociated species [= rate of formation of H(ads)] determines the rate. It is probable that H(ads) reacts very rapidly as soon as it is formed with associatively adsorbed ethene; none was lost to the gas phase as $H_2(g)$ nor to the metal as CsH(s).

A characteristic of the liquid alkali-metals, and of Cs in particular with the lowest work function, is that their chemistry is dominated by electron donation to form ionic compounds. By adopting the concept illustrated in Refs. (*3*) and (*4*) for catalysis on liquid metals, a correlation can be found between the relative lethargy of dissociative adsorption and the energetics of donation of electrons to molecular orbitals on C_2H_4. The photoelectron spectrum of C_2H_4 (*5*) shows that the HOMO ψ_6 (πC=C) has ionisation energy of 1012 kJ mol^{-1} (*6*). The ultraviolet absorption at 171 nm indicates that the LUMO ψ_7 (π^*C=C) is probably at 316 kJ mol^{-1}. Thus electron donation from the HOMO of Cs (work function of 206 kJ mol^{-1} (*7*)) is favourable and encourages associative adsorption (weakening of the C=C bond). Although the energies of the next unoccupied levels ψ_8, ψ_9 (π^*C–H) are unknown, their ionisation energies are expected to be less than that of ψ_7 (*6*), making electron transfer to them and hence dissociative adsorption (weakening of the C–H bond) less favourable. The apparently energetically favourable associative adsorption of C_2H_4 argues against the alternative mechanism where gaseous C_2H_4 reacts directly with H(ads).

The catalytic hydrogenation of C_2H_4.

Mixtures of C_2H_4 with H_2 (1 : 1 and 1 : 2) at 20 kN m^{-2} pressure were exposed to liquid Cs at temperatures between 349 and 418 K, and the concentration of C_2H_4 and the H_2 was determined as before as a function of time. The total pressure invariably fell to one-half of its original value (Table 1) for the 1 : 1 mixtures, and all of the C_2H_4 was converted to C_2H_6:

$$C_2H_4 + H_2 \xrightarrow{Cs} C_2H_6. \quad (2)$$

TABLE 1

Stoichiometry of the Reactions of (a) C_2H_4 with Cs, (b) C_2H_4 with H_2 on Cs, and (c) C_2H_4 with $2H_2$ on Cs

a		b		c	
Temp. (K)	$p_{C_2H_6}:p_{C_2H_4}$	Temp. (K)	$p_{C_2H_6}:p_{C_2H_4}$	Temp. (K)	$p_{C_2H_6}:p_{C_2H_4}$
363	0.67	363	0.50	349	0.32
418	0.67	383	0.49	363	0.34
431	0.67	404	0.50	393	0.33
452	0.67	421	0.50	420	0.31
462	0.68				
477	0.65				
489	0.67				

With the 1 : 2 mixtures, the total pressure also fell smoothly, but ultimately to one-third of its original value (Table 1) according to

$$C_2H_4 + 2H_2 \xrightarrow{Cs} C_2H_6 + 2CsH. \quad (3)$$

In this case the C_2H_4 was again quantitatively hydrogenated to C_2H_6, and the remaining H_2 was converted to CsH. The solid product was not identified directly but heating the metal under vacuum released gaseous H_2 which is characteristic of CsH. Although there was competition for H_2, the C_2H_4 was preferentially reduced to C_2H_6. Again, there was no formation of Cs_2C_2 so that self-hydrogenation was inhibited completely.

Kinetics

The self-hydrogenation of C_2H_4 on Cs followed first-order kinetics; the rate of loss of C_2H_4 decreased with decreasing pressure and plots of log $P_{C_2H_4}$ vs time were linear. The slopes gave the rate constants, k_p. A more quantitative and useful rate constant, k, is that which includes terms for gas volumes (moles) and surface area of metal as shown by

$$k = \frac{dV}{dt_{STP}} \cdot \frac{1}{S} \cdot \frac{1}{P}$$

$$= \frac{273}{101325}\left[\frac{V_1}{T} + \frac{V_2}{298}\right]\frac{k_p}{S} \cdot \frac{P}{P}$$

$$= \frac{273}{101325}\left[\frac{V_1}{T} + \frac{V_2}{298}\right]\frac{k_p}{S}, \quad (4)$$

where V_1 and V_2 are the hot (112,420) and cold (49,880) volumes (mm^3), respectively, of gas; S is the surface area (1476 mm^2) of metal presented to the gas at any instant; T is the reaction temperature (K) and k_p is the pressure-dependent rate constant (s^{-1}). The surface area of metal exposed to the gas at any instant was calculated from the diameter and length of the liquid jet, the dimensions of the cascade, and the diameter of the liquid pool below. Variations in pumping speed above a minimum produce only a marginal increase in rates, and when solids are formed these are swept to the side leaving fresh metal exposed to the gas. Values of k are given in Table 2.

TABLE 2

Rate Constants $k[mm^3_{STP}\ s^{-1}\ mm^{-2}\ (N\ m^{-2})^{-1}]$ for the Self-hydrogenation and Catalytic Hydrogenation of C_2H_4 on Liquid Cs

C_2H_4			$C_2H_4 + H_2$			$C_2H_4 + 2H_2$		
T (K)	10^4k_p (s^{-1})	10^8k	T (K)	10^4k_p (s^{-1})	10^8k	T (K)	10^4k_p (s^{-1})	10^8k
363	3.53	30.7	363	0.97	8.45	349	0.88	7.86
418	5.77	46.0	383	1.70	14.3	363	1.72	15.0
431	6.54	51.1	404	4.88	39.7	393	4.62	35.2
452	7.31	55.5	421	6.79	53.4	420	10.04	79.7
462	7.62	57.1						
477	11.1	81.7						
489	11.7	84.8						

The catalytic hydrogenation of C_2H_4 by equimolar quantities of H_2 was also a first-order process and the corresponding rate constants, k, are also collected in Table 2.

A comparison between the systems is achieved by an Arrhenius plot of ln k vs 1/T (Fig. 5). The self-hydrogenation process shows a shallow temperature dependence

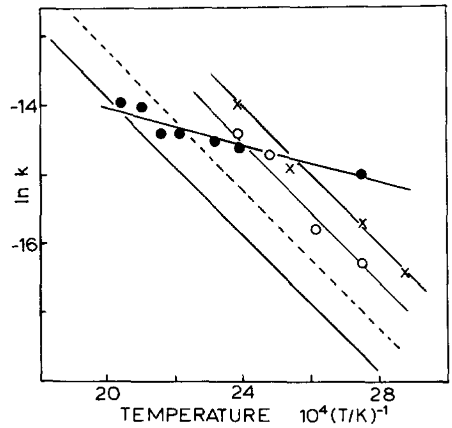

FIG. 5. Rates of reaction. (●) C_2H_4 with Cs, (O) C_2H_4 with H_2 on Cs, (x) C_2H_4 with $2H_2$ on Cs, (—) H_2 with Cs, and (- - -) rate of formation of H(ads) on Cs.

with an apparent activation energy of 15.8 kJ mol^{-1}. This is ostensibly the energy of dissociative adsorption of C_2H_4 on Cs, whereas the pre-exponential factor, A, in the Arrhenius equation $k = A \cdot \exp(-E/RT)$ embodies aspects of the energy of the collisions, the orientation of the C_2H_4 molecules to the surface, and the availability of vacant adsorption sites.

The catalytic hydrogenation shows a higher activation energy of 45.5 kJ mol^{-1} and a significant feature is that it resembles that (42.4) for the H_2 + Cs reaction (*1*). The common value of the activation energy implies that the same rate-determining step is responsible for both the catalytic hydrogenation of C_2H_4 on Cs and the normal reaction of H_2 with Cs. The latter has been attributed (*1*) to the conversion of H_2 to adsorbed H atoms (Fig. 4d), and so the mechanism is the reduction of the associatively adsorbed alkene by adsorbed H atoms produced from the dissociation of H_2 at the metal surface. Verification of the mechanism comes from a comparison of the rate of generation with the rate of loss of H(ads). The rate of formation of H(ads) is twice the rate constant for the H_2/Cs reaction. The rate of loss of H(ads) is half the rate constant for the H_2/C_2H_4 reaction since every C_2H_4 uses 2H(ads). The agreement between the values (Fig. 5, dashed line), verifies that the rate of formation of C_2H_6 from C_2H_4 is governed by the rate of generation of H(ads) from the H_2/Cs reaction.

An increase in the proportion of H_2 to 2 : 1 caused a more rapid loss of C_2H_4. The plots of ln (P/P_0) were linear except toward the end of the absorption. The rate constants, k, are generally greater than those for the 1 : 1 mixtures (Table 2). They could be assigned the same temperature dependence (activation energy) as that of the 1 : 1 mixture. The smoothed values show that doubling the H_2 pressure nearly doubles the rate of reaction of C_2H_4. The rate of catalytic hydrogenation appears to depend only on the pressure of H_2 so the process is zero order with respect to C_2H_4 and first order w.r.t. H_2,

$$-dP_c/dt = k_p P_c^0 P_H^1. \quad (5)$$

The increase in rate of hydrogenation with increase in pressure of H_2 (P_H) can be attributed to the increase in rate of formation of H(ads) (Fig. 4d).

Comparison with Other Work

Hill and Kistiakowsky (*8*) exposed $C_2H_4 : H_2$ mixtures to static Cs up to 473K and found increasing amounts of C_2H_6 with increasing temperature. A film of CsH progressively curtailed the reaction but separate experiments showed that CsH converted C_2H_4 to C_2H_6 very slowly. The rates were not quantified. Self-hydrogenation of C_2H_4 on liquid Cs is similar to that on liquid K (*2*) and liquid Na (*9*) under the same conditions except that progressively higher temperatures are needed to promote the reaction. Similarly, higher temperatures are needed to promote catalytic hydrogenation of C_2H_4 on K. No rates were measured but equimolar quantities of C_2H_4 and H_2 on K produced eventually $C_2H_6 : C_2H_4$ ratios of 0.94, 0.96, 0.98, and 0.94 : 1, at 538, 568, 588, and 604 K, respectively (*2*). On liquid Li, the degree of self-hydrogenation is severely reduced and the metal converts the alkene to Li_2C_2 and LiH (*9*). Thus the ability to self-hydrogenate diminishes in the order Cs > K > Na > Li and can be attributed to the increasing thermodynamic stability of the solid products M_2C_2 and MH. These compounds are least stable for M = Cs, implying that the relevant intermediates in their formation are sufficiently weakly adsorbed to allow both maximum self-hydrogenation and catalytic hydrogenation of the alkene. The ability of Cs to donate electrons into the LUMO of C_2H_4 and weaken the C–H bond should not be unique. Other unsaturated species such as C_2H_2, conjugated hydrocarbons, aromatic molecules, as well as C≡O and C≡N moieties might be similarly activated by the liquid Cs surface and hence rendered susceptible to catalytic hydrogenation.

ACKNOWLEDGMENT

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