Reaction of Ethylene at the Surface of Liquid Potassium

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The reaction of ethylene with liquid potassium has been investigated from 503 to 671 K by pressure changes and gas analysis as the metal is injected in to the gas by means of an electromagnetic pump. At the lower temperatures self hydrogenation occurs precisely according to $3C_2H_4 \longrightarrow 2C_2H_6 + 2C$ (or K_2C_2). The surface reaction is explained by dissociative adsorption of ethylene in to hydrogen adatoms which are subsequently employed in hydrogenation. With increasing temperature progressively less ethane is produced which is attributed to loss of hydrogen from the surface by solution in the metal. The Arrhenius plot for the reaction is not linear over the whole temperature range, a feature which is accounted for by differences in the rates of dissociation and hydrogenation.

THIS work forms part of a study of the reactions of hydrocarbons at liquid alkali-metal surfaces. Previously the reactions of acetylene and propyne with sodium have been described [1] and also those of acetylene and ethylene with dilute solutions of barium in sodium.[2] Acetylene produces ethylene and hydrogen with sodium but, whereas the metal is relatively inert towards ethylene, addition of barium substantially increases the reactivity. We find potassium reacts with ethylene to form ethane and these first experiments with this metal show a distinct similarity to the reaction of propyne with sodium in that, under the appropriate conditions, maximum possible efficiency in self hydrogenation at the metal surface is achieved.

EXPERIMENTAL

Ethylene (99.8%, B.D.H.) was used without further purification. The major impurity was methane which is inert towards potassium under the present experimental conditions. Potassium was purified by filtration directly into the stainless-steel apparatus, described previously,[3] under a protective atmosphere of argon. In the present apparatus, liquid potassium was drawn from the bulk by a small d.c. electromagnetic pump and ejected into the gas as a horizontal jet. Under these conditions the gas reacted with a continuously regenerated clean metal surface. The assembly was enclosed in a heated cabinet and attached to a low-volume manometer and vacuum frame.

Procedure.—The reaction vessel was brought up to the required temperature and evacuated to 0.010 N m^{-2} to remove argon. The liquid metal was circulated and ethylene admitted to the required pressure. The progress of the reaction was followed by pressure changes and by gas analysis. At selected times the entire gas mixture was frozen out into a sampling tube. The gas was diluted with air and analysed by means of a gas–liquid chromatograph (Pye, series 104). The separating column (3.6 m, diameter 4 mm) was packed with squalane (25% w/w) on a 30—60 mesh silocel C22 support and was run at 323 K. A flame-ionisation detector was used to monitor the constituents. The last traces of gas in the reaction vessel were pumped off and the next volume of ethylene admitted. The procedure was then repeated at different temperatures.

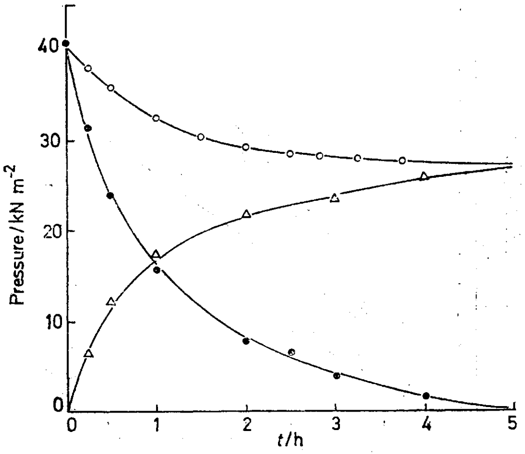

FIGURE 1 Partial pressures of ethylene and ethane in the reaction of the olefin with liquid potassium at 568 K: (○), total pressure; (△), ethylene gain; (●), ethylene loss

RESULTS AND DISCUSSION

Reaction Products.—The reaction was studied at 10 temperatures in the range 503—671 K. Starting pressures were between 53.55 and 37.72 kN m^{-2}. The pressure decreased smoothly to a constant finite value in all experiments as shown in Figure 1 for 568 K in which the

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[1] C. C. Addison, M. R. Hobdell, and R. J. Pulham, *J. Chem. Soc.* (*A*), 1971, 1704.

[2] C. C. Addison, M. R. Hobdell, and R. J. Pulham, *J. Chem. Soc.* (*A*), 1971, 1708.

[3] G. Parry and R. J. Pulham, *J.C.S. Dalton*, 1975, 446.

decrease was complete in 5 h. The sole gaseous product at all stages and temperatures was ethane. At intermediate stages in the reaction the gaseous mixture was all condensable at liquid-nitrogen temperature, 77 K, which excluded the presence of hydrogen, and analysis by g.l.c. showed the mixture to be ethane and unchanged ethylene.

The solid product was identified by chemical and X-ray analysis as carbon at 620 K, but formation of potassium acetylide, K_2C_2, at the lower temperatures was indicated since hydrolysis by water vapour at the metal surface produced some acetylene. The acetylide probably originates from the reaction of ethylene with the metal rather than from a subsequent metal–carbon reaction. It seems remarkable that K_2C_2 has not been characterised since first reported by Moissan in 1903. Although the thermal stability is uncertain, the present data are consistent with decomposition to the elements with increasing temperature at low pressure as for Na_2C_2.[4] The hydrogen balance showed that the related potassium hydrogenacetylide, $K(C_2H)$, could not have been formed.

Reaction Stoicheiometry.—Up to 568 K two molecules of ethane were produced for every three molecules of ethylene consumed [equation (1)]. The reaction can be

$$3C_2H_4(g) \longrightarrow 2C_2H_6(g) + 2C(s)\ (\text{or } K_2C_2) \qquad (1)$$

divided into two parts, dissociation of ethylene and its self hydrogenation. In view of the electropositive nature of potassium and the detection of the acetylide ion, C_2^{2-}, it is feasible that transfer of electrons from the conduction band of the metal to the ethylene molecule occurs at the surface with the elimination of hydrogen atoms which are immediately chemisorbed [equation (2)]. There is

$$\begin{tikzcd} C_2H_4(g) \arrow[r, "2e^-"] & HC{=}CH^{2-} + 2H\,(ads) \arrow[r] & C{\equiv}C^{2-} + 4\,H(ads) \arrow[d, "-2e^-"] \\ & & 2C \end{tikzcd} \qquad (2)$$

no known potassium compound containing the $HC{=}CH^{2-}$ ion, but this step features in the hydrogenation of ethylene on a nickel surface with which the potassium reaction shows considerable similarity. On nickel the initial step has been ascribed [5] to dissociative adsorption where the olefin undergoes two-point adsorption at room temperature with fission of the carbon–hydrogen bond [equation (3)]. Although it has been suggested [6] that

$$C_2H_4(g) \longrightarrow \underset{*}{H}\underset{*}{C}{=}\underset{*}{C}H + \underset{*}{H} + \underset{*}{H} \qquad (3)$$

adsorption takes place by an associative mechanism in which opening of the double bond occurs, subsequent work [7,8] supports an alternative dissociation process. It appears from i.r. spectroscopy that adsorption can occur by either mechanism depending on the temperature, but the associative process is not favoured unless hydrogen is preadsorbed.[9] In the reaction of ethylene with silica-supported nickel the spectra indicate that the adsorbed stable species are of the σ-bonded type, such as $NiCH_2$-CH_2Ni, $NiCH{=}CHNi$, $Ni_2CHCHNi_2$, and a C_2 surface carbide.[10]

Each dissociated ethylene molecule provides four adsorbed hydrogen atoms [equation (2)]. These are all used in the hydrogenation of ethylene and none is lost as potassium hydride or molecular hydrogen. The observed 2 : 3 stoicheiometry [equation (1)] clearly represents maximum possible efficiency in self hydrogenation which would be achieved by a rapid hydrogenation process such as that shown in equation (4).

$$2\,H(ads) + C_2H_4(g) \longrightarrow C_2H_6(g) \qquad (4)$$

With mixtures of hydrogen and ethylene the reaction between adsorbed hydrogen atoms and gaseous ethylene [equation (4)] has been considered to be too rapid to be rate controlling on nickel, but possibly rate controlling on tungsten where the apparent activation energy is 10.5 kJ mol^{-1}.[5] The self hydrogenation of ethylene to ethane on nickel proceeds with the comparable apparent activation energy of 12.6 kJ mol^{-1} below 273 K and for this reason the rate-controlling step on nickel has been assigned [11] to equation (4) rather than the surface-recombination reaction (5) which proceeds on nickel with the higher activation energy of 44.9 kJ mol^{-1}.[5]

$$\underset{*}{H}\underset{*}{C}{=}\underset{*}{C}H + 4\,\underset{*}{H} \longrightarrow C_2H_6(g) \qquad (5)$$

Ethane liberated at the potassium surface was inert towards the metal. There was no evidence from the g.l.c. analyses that the hydrocarbon was subsequently converted to methane at least up to 671 K. This contrasts with nickel where at 473 K methane was the sole gaseous product and corresponded to progressive conversion of the adsorbed residue, $H\underset{*}{C}{=}\underset{*}{C}H$, into carbide or carbon. The carbonised solid surface prevents virtually all hydrogenation to ethane and, if the latter is introduced at this stage, cracking to methane occurs. With liquid potassium, however, although carbon is formed, fresh metal is exposed at least up to 671 K for continuous self hydrogenation, which is completely efficient up to 568 K.

With increasing temperature the stoicheiometry departed from the 2 : 3 ratio, and progressively less ethane was produced. This effect was greater, moreover, when larger masses of metal were used even though the area of metal presented for reaction remained constant. This is shown in Figure 2 where the molar ratio of ethane produced to ethylene consumed is presented as a function of temperature for different quantities of metal. Up to *ca.* 568 K neither temperature nor quantity of metal had much effect on the 2 : 3 stoicheiometry [line (*a*)]. At

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[4] C. C. Addison, M. R. Hobdell, and R. J. Pulham, *J. Chem. Soc.* (*A*), 1971, 1700.

[5] O. Beeck, *Discuss. Faraday Soc.*, 1950, **8**, 118.

[6] G. H. Twigg and E. Rideal, *Proc. Roy. Soc.*, 1939, **A171**, 55.

[7] G. I. Jenkins and E. Rideal, *J. Chem. Soc.*, 1955, 2490.

[8] S. J. Stephens, *J. Phys. Chem.*, 1958, **62**, 714.

[9] R. P. Eischens, *Adv. Catalysis*, 1958, **10**, 1.

[10] N. Sheppard, N. R. Avery, B. A. Morrow, and R. P. Young, 'Chemisorption and Catalysis,' ed. P. Hepple, Institute of Petroleum, London 1971, p. 135.

[11] D. W. McKee, *J. Amer. Chem. Soc.*, 1962, **84**, 1109.

higher temperatures, however, progressive diminution in the yield of ethane occurred with increasing temperature for a given mass of metal [curve (*b*)]. The yield decreased even further when more metal was used [curves (*c*)—(*e*)].

The decreasing efficiency in the self-hydrogenation can be attributed to competition for hydrogen by the metal. The rate of reaction of potassium with hydrogen to form potassium hydride increases exponentially with increasing temperature [3] and this is coupled with a likewise increasing solubility of hydride.[12] These features are shown in the lower part of Figure 2. Solubility data are not available at all relevant temperatures so that extrapolated values are shown below 613 K. With increasing temperature, therefore, progressively more adsorbed hydrogen forms hydride which dissolves, thereby restricting hydrogenation, Ethylene encounters a hydrogen-deficient surface and therefore carbon is formed rather than ethane. This is enhanced when more metal is used since more hydrogen is drawn from the surface into solution.

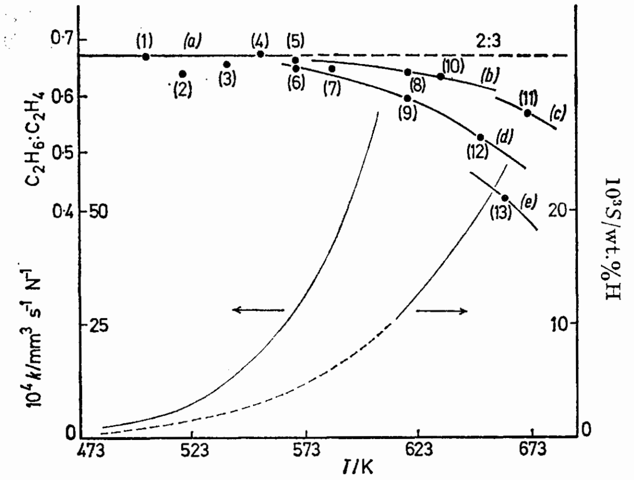

FIGURE 2 Molar ratio of ethane produced to ethylene consumed on liquid potassium at various temperatures. The quantities of metal employed (moles metal : moles C_2H_4) were: (1), 887; (2), 435; (3), 373; (4), 405; (5), 351; (6), 952; (7), 569; (8), 585; (9), 989; (10), 630; (11), 668; (12), 952, and (13), 2 091. The rate of reaction of hydrogen and its solubility are shown below

Auxiliary Experiments.—(i) *Hydrogen desorption*. Dissolved hydrogen is still potentially capable of reducing ethylene but only slowly, since desorption from solution is gradual. That hydrogen had dissolved and was slowly desorbed was shown separately. After all the ethylene had been consumed in a reaction at 671 K, the residual ethane was quickly pumped off and the vessel sealed. There was slow evolution of gas from the metal to create an equilibrium pressure. The gas contained no hydrocarbon and was not condensable at 77 K. In the absence of ethylene, therefore, desorbed hydrogen atoms formed molecular hydrogen in the normal fashion to establish the equilibria in equation (6).

$$H^-(s) \rightleftharpoons H^-(soln) \underset{e^-}{\rightleftharpoons} H(ads) \rightleftharpoons \tfrac{1}{2} H_2(g) \qquad (6)$$

(ii) *Hydride-saturated metal*. When the metal is saturated with hydride then hydrogenation is more extensive. This was shown by experiments in which potassium was pretreated with more than enough hydrogen to saturate the liquid. When all admitted hydrogen had been absorbed ethylene was introduced and the reaction followed as before. At 505, 537, 568, and 604 K the final molar ratio $C_2H_6 : C_2H_4$ was 0.77, 0.80, 0.86, and 0.80 : 1, respectively. Thus, when removal of hydrogen atoms from the surface is suppressed by prior saturation of the liquid, hydrogenation predominates, and since these ratios are greater than the 0.67 : 1 obtained previously the excess of potassium hydride also supplements hydrogenation. This is expected from the equilibria in equation (6).

(iii) *Mixtures of ethylene and hydrogen*. The preceding experiments suggest that provision of adsorbed hydrogen in excess of that available from ethylene should enhance hydrogenation. In four further experiments hydrogen in equimolar proportions with ethylene was treated with potassium as before. The mixture is stable, of course, in the absence of potassium. Hydrogenation again occurred at the metal surface and at 538, 568, 588, and 604 K the ratio $C_2H_6 : C_2H_4$ was 0.94, 0.96, 0.98, and 0.94 : 1, respectively. The extent of hydrogenation was much higher (approaching 100%) than in other experiments, and is attributed to copious formation of hydrogen adatoms from molecular hydrogen.

Comparison with Sodium.—There are several related features in the reactions of potassium and sodium with hydrocarbons. The reaction of ethylene with potassium resembles that of acetylene with liquid sodium in that self hydrogenation occurs to produce some ethylene, but, in the presence of the very strongly adsorbed acetylene, hydrogen is desorbed in to the gas phase and, though normally capable of reacting with the metal, remains until all the acetylene has reacted. Ethylene is inert to sodium at low temperatures in contrast to potassium, but reacts with solutions of barium in sodium. Dissociation of ethylene again occurs but hydrogenation is slight and no gaseous hydrogen is produced. Carbide and hydride are formed rather than ethane. This is consistent with strong adsorption of both ethylene and hydrogen, and the formation of thermally stable barium hydride.

The closest analogy with the present work is found in the reaction of propyne with sodium. At 383 K the ratio of propene produced to propyne consumed is precisely 1 : 3 compared with the 2 : 3 ratio ethane : ethylene we find. It appears, therefore, that the maximum possible efficiency in self hydrogenation is achieved in these two cases and this occurs when reactant and hydrogen atoms are equally weakly adsorbed, hydrogenation is rapid, and hydrogen is not lost by dissolution in the liquid-metal substrate.

Kinetics.—The fall in partial pressure (p) of ethylene

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[12] M. N. Arnol'dov, M. N. Ivanovskii, V. A. Morozov, S. S. Pletenets, and V. V. Sitnikov, *Proc. Acad. Sci.* (*U.S.S.R.*), *Metals*, 1973, **1**, 74.

with time (shown typically in Figure 1) was used to determine the rate of reaction in all experiments. Plots of $\ln p$ against time were linear at all temperatures showing that the rate of reaction was directly proportional to the ethylene pressure [equation (7)] and hence was first order in its concentration. Rate constants, k, were

$$-dp/dt = k_p p \text{ or } -\ln p = k_p t + C \qquad (7)$$

calculated from equation (8) where dV/dt is the volume

$$k = (dV/dt)S^{-1}p^{-1} \qquad (8)$$

(mm^3 at n.t.p.) absorbed per second at pressure p (kN m^{-2}) and S is the surface area (mm^2) of metal.

The rate constant did not increase regularly with increasing temperature. The variation is shown by the Arrhenius plot of $\ln k$ against T^{-1} in Figure 3. From 503 to *ca.* 568 K the rate increased rapidly with increasing temperature but thereafter increased in accord with the Arrhenius equation but much less rapidly. These results indicate a change in rate-controlling process with increasing temperature. Ethylene consumption is very slow below 568 K and whereas hydrogenation by adatoms is probably rapid [equation (4)] the dissociation of ethylene [equation (2)] might be slower and control the rate in this region. Until this occurs hydrogenation cannot proceed, but when able does so with maximum efficiency. This premise is supported by rates from the auxiliary experiment (ii). When the hydrogen-atom concentration was augmented, ethylene was consumed more rapidly at the lower temperatures as shown by the open circles in Figure 3. These approach the extrapolated (broken line) high-temperature rates and are consistent with rapid hydrogenation. Above 568 K, however, although extra hydrogen increased the amount of ethane formed it had no effect on the rate of disappearance of ethylene, indicating that hydrogenation was rate controlling. The linear section provides an apparent activation energy of 27.7 kJ mol^{-1}, ostensibly for the hydrogenation process. There are no other data reported for alkali metals for comparison.

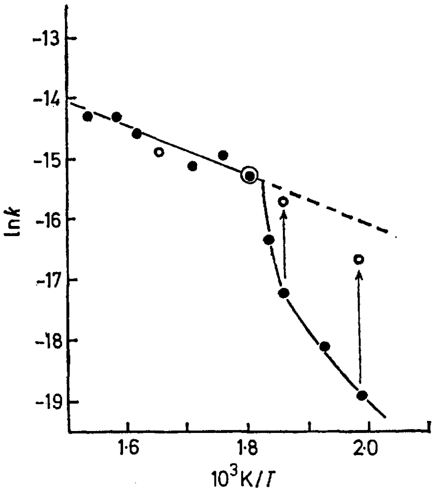

FIGURE 3 Arrhenius plot for the reaction of ethylene with potassium: (●), pure metal; (○), metal presaturated with hydrogen

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