[CONTRIBUTION FROM THE LABORATORIUM VOOR PHYSISCHE SCHEIKUNDE DER UNIVERSITEIT TE LEUVEN (LOUVAIN)]

The Catalytic Interaction of Hydrogen and Deuterium with Ethylene and Deutero-ethylenes on Copper

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Numerous efforts have been made to elucidate the detailed mechanism of the catalytic hydrogenation of ethylene by studies of the kinetics of interaction of ethylene with hydrogen and deuterium.[4] The possibility of a more penetrating analysis of the problem presented itself to us in the preparation of ethylene-d_4 and various deuterium-substituted ethylenes, permitting therefore catalytic studies in which the effect of the substitution of the unsaturated partner in the hydrogenation process could be tested independently with both hydrogen and deuterium as the addition agents.

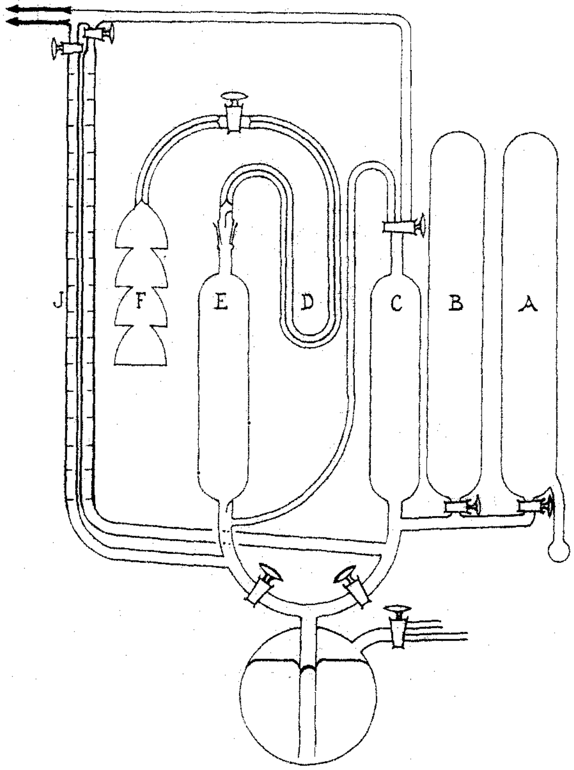

Fig. 1.

Experimental Details

Gases. Ethylene was obtained by the interaction of ethyl alcohol and sulfuric acid. The gas was freed from ether and acid fumes in the usual way and purified by liquefaction and fractionation. It was stored in a reservoir in the reaction system (Fig. 1) in which the process of condensation and removal of volatile impurities could be repeated at intervals if necessary.

Ethylene-d_4 was obtained by the action of zinc on ethylene dibromide-d_4 prepared by interaction of acetylene-d_2 and deuterium bromide. The acetylene-d_2 was prepared by interaction of 99.6% deuterium oxide with a high grade calcium carbide, freed from water by heating at 500° for several hours. The deuterium bromide was prepared by the hydrolysis of resublimed phosphorus pentabromide with 99.6% deuterium oxide. The ethylene-d_4 was purified by vacuum distillation and the middle fraction (6 liters) was admitted to a reaction reservoir, A, the walls of which had been covered with molten sodium to eliminate traces of bromine compounds which might have survived the purification process. Raman spectra observations of this product indicate that it is 90–95% C_2D_4 or better than 97.5% deuterium content of the hydrogen of the hydrocarbon.

Ethylene-d_2 was obtained by catalytic exchange between ethylene and deuterium oxide on an active nickel catalyst at 150° during several days. The central fraction of 6 liters from the purification process showed, by Raman spectra, that its D-content was slightly greater than 50%, and that it was composed predominantly of symmetrical *cis*- and *trans*-$C_2H_2D_2$, with much smaller amounts of the unsymmetrical $CH_2{=}CD_2$ and C_2H_3D and C_2HD_3.

The hydrogen and deuterium were obtained by electrolysis of appropriate solutions of NaOH and NaOD. The gases were purified over hot copper, dried over phosphorus pentoxide and liquid air and stored in receptacles of Type B. Some hydrogen used was further purified by adsorption on and desorption from charcoal.

Catalysts.—The copper catalyst employed was prepared by dehydration and reduction of a co-precipitated mixture of magnesium hydroxide–copper hydroxide in the molecular ratio 4:1 whose catalytic characteristics have been described already by Taylor and Joris.[5] In many of the experiments only 0.5 g. of catalyst, corresponding to 0.11 g. copper, was employed. In some of the last experiments 4 g. of the catalyst was used.

Apparatus.—The reaction vessel F (85-cc. volume) shown in Fig. 1 was of a shape which permitted the distribution of the catalyst on the horizontal areas of the several "stories," thus providing greater accessibility of catalyst to gas mixture. Gas mixtures were prepared in E, from the storage reservoirs, A and B, via the vessel C. The gases were introduced into the reaction vessel by raising the

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[4] (a) Farkas, Farkas and Rideal, *Proc. Roy. Soc.* (London), **A146**, 630 (1934); (b) Klar, *Z. physik. Chem.*, **B27**, 317 (1934); *Z. Elektrochem.*, **43**, 379 (1937); (c) Pease and Wheeler, THIS JOURNAL, **57**, 1149 (1935); (d) Farkas and Farkas, *Trans. Faraday Soc.*, **33**, 678, 827 (1937); THIS JOURNAL, **60**, 22 (1938).

[5] Taylor and Joris, *Bull. soc. chim. Belg.*, **46**, 241 (1937).

mercury level in E, the gases passing through the trap D cooled in solid carbon dioxide–acetone mixtures to minimize access of mercury vapor to the catalyst system. During reaction, the mercury level was maintained at the glass point near the entrance to the capillary tubing, pressures, at constant volume, being read on the manometers J, through which, also, the apparatus could be evacuated. Between experiments, the catalyst was evacuated to a pressure of 10^{-4} mm. at the temperature of the succeeding experiment if above that of the preceding.

Procedure.—Experiments have been performed at −20, 0, 20 and 40°. The gas ratios studied were 1:1, 2:1 and 1:2, the unit pressure being 5 cm. for each component, 10 cm. for the constituent in excess in the non-stoichiometric mixtures.

Experimental Results

With the smaller amount of catalyst first used a small drift was noted in catalyst activity. The data have been presented graphically in Figs. 2–6, in small groups covering a particular variable to be investigated and in a sequence such that any variation due to the observed fatigue of the catalyst would be minimized in its effect on the conclusions to be drawn.

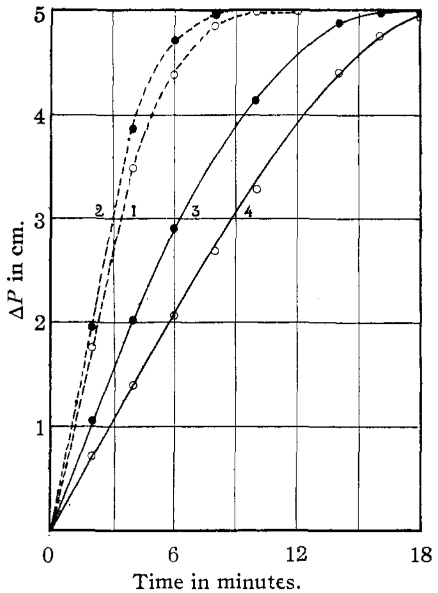

Fig. 2.—Experiments at 40° (5 cm., 5 cm.): 1, $C_2H_4 + H_2$ (40° 3); 2, $C_2D_4 + H_2$ (40° 2); 3, $C_2D_4 + D_2$ (40° 2); 4, $C_2H_4 + H_2$ (40° 3).

Note on Figs. 2–8.—Dotted lines indicate hydrogenation; full lines indicate deuterization. Circles indicate C_2H_4; dots indicate C_2D_4.

In Fig. 2 are presented the data on stoichiometric mixtures of the four gases taken in pairs in the order shown, reacting at 40°. These experiments show unquestionably (a) that ethylene-d_4 hydrogenates more rapidly than ethylene and (b) that the rate of reaction of both with deuterium is approximately one-half that with hydrogen. This latter result confirms that of Pease and Wheeler[4c] on a different but active copper catalyst.

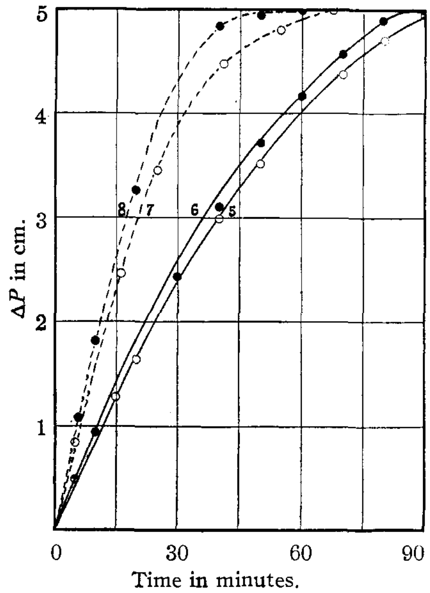

Fig. 3.—Experiments at 20°: 5, $C_2H_4 + D_2$; 6, $C_2D_4 + D_2$; 7, $C_2H_4 + H_2$; 8, $C_2D_4 + H_2$.

The data of Fig. 3 confirm both these conclusions for stoichiometric pairs of gases at 20°. The data with hydrogen are comparable with those at 40°. With deuterium the spread between the two ethylenes is less than at 40° but this is probably largely experimental error and, even in this case, ethylene-d_4 is still a faster reactant than ethylene.

Experiments 11–14 at 40° in Fig. 4 once more confirm these results and supply data on varying rate with varying concentration. The reaction is faster than that of the stoichiometric mixture in presence of excess deuterium and markedly slower with excess of the ethylenes. In the latter cases, also, the change in rate with time is much greater than with the stoichiometric mixtures. This is also shown by the data of Experiments 15–17 in Fig. 5, the rates of 16 and 17 again pointing to a reaction with deuterium somewhat less than half that with hydrogen.

The data of Experiments 20–23 at 40° presented in Fig. 6 show that the 50% D-substituted ethylene reacts at a rate intermediate to that of ethyl-

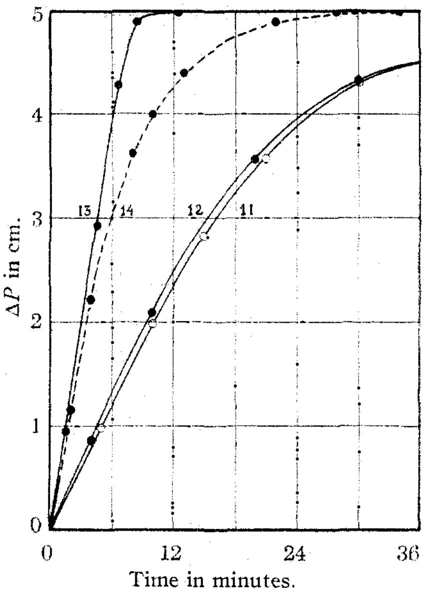

Fig. 4.—Experiments at 40°: 11, $2C_2H_4 + D_2$ (10 cm. C_2H_4 + 5 cm. D_2); 12, $2C_2D_4 + D_2$ (10 cm. C_2D_4 + 5 cm. D_2); 13, $C_2D_4 + 2D_2$ (5 cm. C_2D_4 + 10 cm. D_2); 14, $2C_2D_4 + H_2$ (10 cm. C_2D_4 + 5 cm. H_2).

ene and ethylene-d_4. A comparison of Experiments 20 and 23 gives an indication of the degree of reproducibility attainable in separated runs. At 0° the same influence of extent of deuterium substitution on the velocity is found.

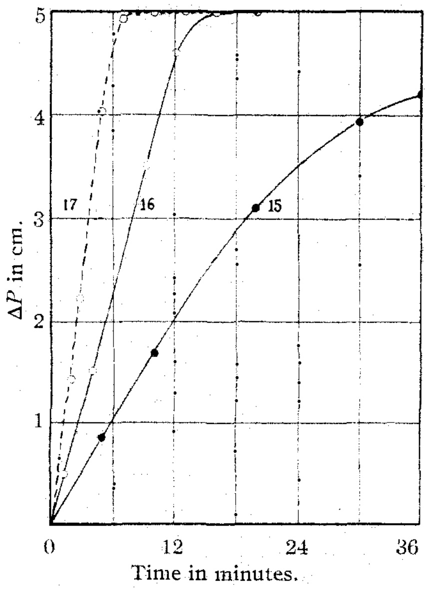

Fig. 5.—Experiments at 40°: 15, 10 cm. $C_2D_4 + D_2$; 16, 5 cm. $C_2H_4 + 2D_2$; 17, 5 cm. $C_2H_4 + 2H_2$.

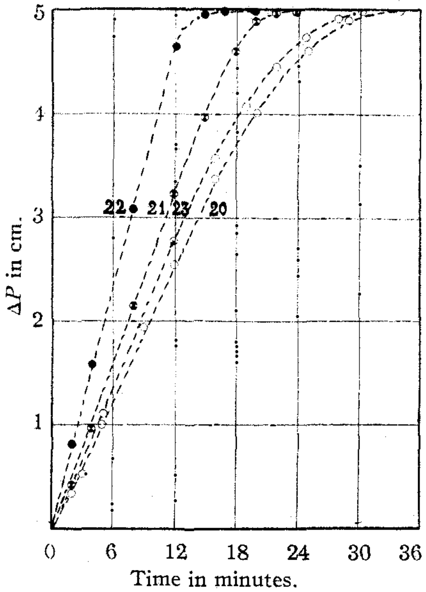

Fig. 6.—Experiments at 40°: 20, $C_2H_4 + H_2$; 21, $C_2(DH)_2 + H_2$; 22, $C_2D_4 + H_2$; 23, $C_2H_4 + H_2$.

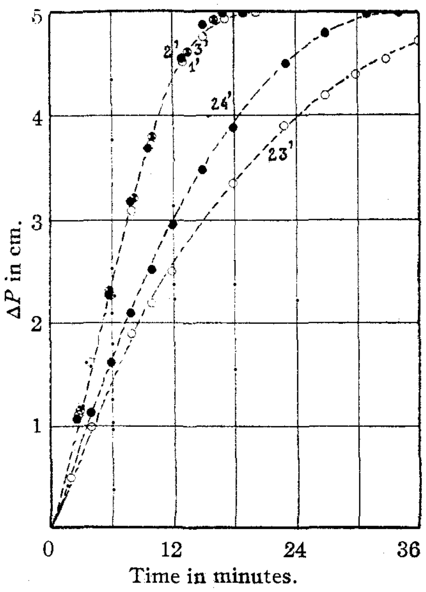

Fig. 7.—At 20°, influence of deterioration P, 5 cm.: 1', $C_2H_4 + H_2$; 2', $C_2(HD)_2 + H_2$; 3', $C_2D_4 + H_2$; 23', $C_2H_4 + H_2$; 24', $C_2D_4 + H_2$.

To test the effect of catalyst deterioration on the results obtained, a new series of experiments was carried out with 4 g. of the copper oxide–magnesium oxide mixture as source of catalyst mass. In Fig. 7 are presented the data of the first experiments, Nos. 1, 2 and 3 on the new catalyst at 20° with stoichiometric mixtures of hydrogen and C_2H_4, $C_2(HD)_2$ and C_2D_4, respectively. It will be noted that, initially, within the experimental error, all three ethylenes show the same rate of reaction. During the succeeding twenty experiments the activity of the catalyst showed a slow but progressive deterioration, which was accompanied by a progressive increase in the differences of hydrogenation rate between C_2H_4 and C_2D_4, as shown by Experiments 23 and 24 on the same diagram. With ethylene the half life has increased from six to twelve minutes, while that of ethylene-d_4 has changed from six to nine and one-half minutes. Since Experiment 24 with C_2D_4 succeeds Experiment 23 with C_2H_4 and still shows a faster reaction rate although catalyst activity is slowly decreasing, it is evident that the differences in rates observed with the deteriorating catalyst are a function of the two gases and not wholly to be ascribed to the deterioration process.

This is true also of the data presented in Fig. 8 for the effect of temperature in the range -20 to $+40°$ with the stoichiometric mixtures of C_2H_4 and C_2D_4 with hydrogen. The sequence of temperatures studied was -20, $+20$, 0 and 40°. In every case C_2D_4 was studied after C_2H_4 and except at $-20°$ is, in every case, the faster process. At 0, 20 and 40° the times for one-quarter reaction are, respectively, $T_{1/4}$ = 24, 20, 5.3, 4.6, 1.5 and 1.4 minutes. These data correspond to apparent activation energies of hydrogenation $E_{\text{obsd.}}(C_2H_4) = 11.8$ kcal. and $E_{\text{obsd.}}(C_2D_4) = 11.3$ kcal. In this temperature range, therefore, the differences between C_2H_4 and C_2D_4 decrease with increasing temperature. The differences are real but their trend with temperature may well be within the error of experiment. Since, in this temperature range, the influence of varying gas ratios (Fig. 4) points to a unimolecular reaction with respect to hydrogen, inhibited by ethylene, the observed activation energy $E_{\text{obsd.}}$ is related to the true activation energy E_t by the equations

$$E_{\text{obsd.}(C_2H_4)} = E_{t(C_2H_4)} - \lambda_{H_2} + \lambda_{C_2H_4}$$
$$E_{\text{obsd.}(C_2D_4)} = E_{t(C_2D_4)} - \lambda_{H_2} + \lambda_{C_2D_4}$$

where the λ's refer to the respective heats of adsorption. The small difference in observed activation energies (0.5 kcal.) is divided in some indeterminate manner between the true activation energies and the heats of adsorption of the two ethylenes. Since, in general, one would expect $\lambda_{C_2D_4}$ to be somewhat larger than $\lambda_{C_2H_4}$, it would follow that the true activation energy for the reaction between C_2H_4 and hydrogen would be somewhat more than 0.5 kcal. greater than the true activation energy in the hydrogenation of C_2D_4. As might be expected from this reasoning the rate of hydrogenation of C_2D_4 is actually greater than that of C_2H_4 and the intermediate case, $C_2H_2D_2$, is intermediate between these two extremes. Why the true activation energy should be greater for ethylene than for ethylene-d_4 is not apparent.

We can avoid these difficulties of detailed mechanism by stating the observed facts, quite generally, in terms of the concept of the activated complex. At a given ratio of hydrogen to any of the ethylenes, the rate indicates that the concentration of the activated complex $(C_2H_xD_{6-x})^*$ on the surface is greater, the greater the D-concentration of the complex.

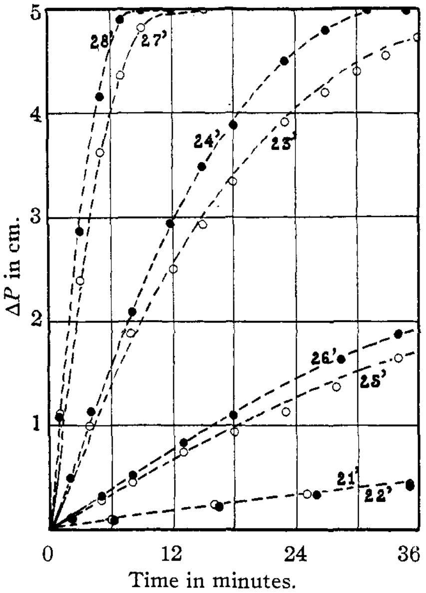

Fig. 8.—Influence of temperature on $H_2 + C_2H_4$ and C_2D_4 (5 cm.): 21′ and 22′ at $-20°$; 25′ and 26′ at 0°; 23′ and 24′ at 20°; 27′ and 28′ at 40°.

This same factor must also be operative in the reactions which involve the comparative rates of reaction between ethylene or ethylene-d_4 and hydrogen or deuterium. With either unsaturated hydrocarbon the velocity of reaction with deuterium is only one-half that with hydrogen. On surfaces largely covered with the unsaturated hydrocarbon, collision rates of hydrogen and deuterium with the free surface would introduce a factor of 1.4 in favor of the hydrogen reaction. What we have termed the concentration of activated complex would, as we have seen, favor more rapid reaction of deuterium by an amount of the order of 10%. It is therefore evident that a definite part of the difference in rates of reaction with hydrogen and with deuterium, approximately one-third of the total difference in rate, is to be ascribed to factors associated with zero-point energy differences of the hydrogen and deuterium, in their interactions with catalyst and substrate. In actual amount these are small, an energy difference of $\Delta E = 250$ cal. being sufficient, together with the collision factor and the concentration of complex, to account for the two-fold difference in velocity observed.

These considerations cannot be decisive in the experiments at −20° (Nos. 21 and 22) where the slow and approximately equal rates with C_2H_4 and C_2D_4 point to the availability of empty spaces for hydrogen adsorption as the rate-determining process.

Since the slow deterioration of the catalyst with time occurs progressively with any of the three ethylenes prepared by three different methods, we cannot ascribe it to impurities in the gases employed. Rather must it be ascribed to progressive irreversible reactions of the ethylenes themselves on the active catalysts which we have employed, leading to carbonaceous deposits on the most active centers, the deposits being retained during the evacuation procedures intervening between experiments. Such deterioration has been well established previously with nickel catalysts, but has not generally been noted hitherto with copper catalysts. The catalysts here used are, as we have already established,[5] very much superior in activity to copper catalysts hitherto studied. It is evident, from the data, that the rate-determining factors change with changes in the active centers studied, the differences between the rates of hydrogenation of C_2H_4, $C_2(HD)_2$ and C_2D_4 being negligible on the most active centers, and definite but relatively small on centers of lesser activity. This again illustrates the observation frequently made that the kinetics of a given heterogeneous surface reaction can vary widely with variation in the surface activity.[6]

Acknowledgment.—We wish to express our indebtedness to Professor Marc de Hemptinne who so kindly placed at our disposal the supplies that we have used of deuterium and of the various deutero-ethylenes.

Summary

1. The rates of addition of hydrogen and of deuterium to ethylene, ethylene-d_2 and ethylene-d_4 on active copper catalysts have been studied in the temperature range −20 to +40°.

2. The addition of deuterium occurs at a rate approximately one-half that of hydrogen on the several ethylenes.

3. Initially, on catalysts of high activity, no differences are observed in the rates of hydrogenation of the several ethylenes.

4. A slow deterioration of the catalyst, ascribed to irreversible reactions of ethylene leading probably to carbonaceous depositions, progressively occurs.

5. With decreasing activity due to this poisoning, small differences in the rates of hydrogenation of the ethylenes are observed, the more highly deuterized ethylenes reacting more rapidly.

6. Collision rates of hydrogen and deuterium with the surface are inadequate to account for the relative rates of addition observed. Zero-point energy differences are also involved.

7. The apparent activation energies of these reactions average 11.5 kcal. in the temperature range studied.

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(6) See, especially, Pease, THIS JOURNAL, **45**, 1196 (1923), for varying kinetic behavior of the reaction $H_2 + C_2H_4$ on copper catalysts of varying activity.