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HYDROGENATION OF ETHYLENE ON METALLIC CATALYSTS

Part 5—On the Deuterium Distribution in Deuteration Products of Ethylene on Evaporated Nickel Film.

By

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Abstract

Temperature dependence of hydrogenation rates of 10 mmHg light ethylene by 10 mmHg protium or deuterium gas on nickel film evaporated at 200°C were observed at temperatures from 0°C to 200°C. The initial products of these deuteration and those at different deuterium partial pressures at 0°C were analyzed by mass spectrometer. Results of the experiments verified our previous theoretical predictions derived from the structure theory of HORIUTI¹⁾ that the predominant evolution of light ethane in deuterioethanes produced by deuteration of light ethylene at temperatures below the optimum switches over to that of dideuteroethane at temperatures above the optimum²⁾ or alternatively at sufficiently high deuterium partial pressure at temperatures below the optimum³⁾.

The ratio of initial rate of hydrogenation by protium to that by deuterium was *ca.* 3.3, 2.0 and 1.0 at 0°C, 50°C and temperatures above the optimum respectively on a fresh film, whereas evenly *ca.* 2.2 on carbided film below the optimum. The optimum temperature and the heat of activation of hydrogenation of equimolar mixture of light ethylene and protium at 20 mmHg total pressure were 105°C and 4.4 Kcal respectively on fresh film, which increased by repetition of runs of similar hydrogenation on the same catalyst surface up to respective steady values of 137°C and 11 Kcal on carbided film. The optimum temperature of deuteration was higher by *ca.* 30°C than that of hydrogenation by protium both on fresh and carbided films.

Introduction

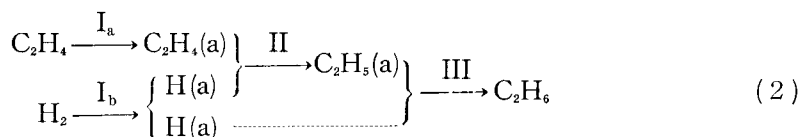
HORIUTI¹⁾ has developed a general theory of the associative mechanism of the reaction



in the presence of metallic catalysts that the reaction follows the sequence of steps

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with the rate-determining step of I_b or III at temperatures below or above the optimum respectively, where (a) signifies an adsorbed state of atoms or atom groups. KEIL²⁾ has deduced on the basis of the above theory the distributions of deuterated hydrogens, ethylenes and ethanes initially formed by catalyzed deuteration of light ethylene, which accounts, on the one hand, for the experimental results of TURKEVICH, SCHISLER and IRSA³⁾ that light ethane predominates over deuterioethanes, and predicts, on the other hand, that dideuterioethane does alternatively at temperatures above the optimum. YATSURUGI and one of the present authors⁴⁾ have previously accounted for on the basis of the same theory the distributions of deuterioethylenes and deuterioethanes at the initial stage of the reaction at -100°C as observed by KEMBALL⁵⁾, and predicted on the same basis that dideuterioethane predominates once again at temperatures below the optimum at sufficient excess of deuterium gas over light ethylene.

In the present work the above two theoretical predictions were qualitatively verified by using mass spectrometrically pure reactants and nickel film evaporated at 200°C , which secured a reproducible condition of the reaction as reported in the previous papers⁶⁾⁷⁾. The latter condition was established in the present experiments by observations of hydrogenation with protium conducted in parallel with those with deuterium, which revealed the isotopic differences in the hydrogenation rate, heat of activation and optimum temperature. The ratio of the rate of hydrogenation with protium to that of deuterium is referred to simply the isotopic effect on hydrogenation rate in what follows. These data were found once again qualitatively in accord with the structure theory.

Experimental

The whole apparatus was the same as that used in the previous work⁶⁾ except an additional train of a pipette of *ca.* 2 cc, sampling vessels of *ca.* 300 cc and a capillary trap cooled by dry ice-alcohol mixture which was connected with the reaction vessel for mass spectrometric analyses of reacted gases. Equimolar mixture of light ethylene and protium or deuterium gas was prepared and stored for the runs of experiment described below, each component being purified similarly as in the previous work⁷⁾⁸⁾ and found mass spectrometrically free from oxygen and nitrogen. The purity of nickel wire used for evaporation was 99.44% as in the previous paper⁷⁾. The catalyst nickel film was coated

at 200°C with freshly evaporated nickel in vacuum of $ca. 1 \times 10^{-6}$ mmHg after the reaction vessel was treated with a few mmHg hydrogen at 500°C and then evacuated at the same temperature as in the previous papers^{6,7)}; the nickel film thus freshly coated is termed simply fresh film in what follows. Volume of the circulation system including the reaction vessel was $ca. 200$ cc and the area covered by the film was $ca. 35$ cm².

Initial rates of hydrogenation with protium (termed protation in what follows) or deuteration were determined by following the total pressure by registering the capacity of an electric condenser consisting of mercury in manometer tube of $ca. 1$ cm diameter and aluminium foil fitted around it by means of an oscillator of 425 Kilocycles and a pen-recorder.

Mass spectrometric analyses of gases were conducted as follows. Reacted gas was admitted from sampling vessel into mass spectrometer through a liquid nitrogen trap and mass spectrum of the reacted hydrogen gas, *i.e.* peaks M_2 , M_3 and M_4 of mass number 2, 3 and 4 respectively, was thus recorded with the electron accelerating voltage V_e of 75 volt, fixing voltages of the focus grids at the maximum height of peak M_4 .

Hydrogen was now evacuated from the sampling system of the mass spectrometer and the trapped hydrocarbon evaporated into it. Mass spectrum consisting of five peaks from M_{26} to M_{30} exclusively of parent ions of deuterioethylenes C_2P_4 , C_2P_3D , $C_2P_2D_2$, C_2PD_3 and C_2D_4 was recorded with V_e of 12 volt. Mass spectrum of ethanes alone was obtained by separating it from ethylenes by brominating them at room temperature and by distilling it from -78°C to liquid nitrogen temperature. The V_e of 14 volt gave a simple spectrum consisting only of two peaks M_{28} and M_{30} for light ethane with a sufficient sensitivity.

The voltage of the focus grids were adjusted in every case of hydrocarbon analyses at the maximum height of M_{28} .

Relative abundance of deuterioethylenes were determined by the relative heights of peaks in the mass spectrum with V_e of 12 volt and those of deuterioethanes were evaluated from their spectrum with V_e of 14 volt by the usual method with reference to theoretical mass spectra of individual deuterioethanes calculated on the basis of the spectrum of light ethane.

Results

Temperature Dependences of the Hydrogenation Rates.

Curve I in Fig. 1 is the ARRHENIUS plot of initial hydrogenation rate of the equimolar mixture of light ethylene and protium or deuterium at 20 mmHg

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initial total pressure of runs each conducted on fresh film and curve II that of runs with the same mixture each carried out after evacuation of gas of the run at the same temperature of curve I to 1×10^{-5} mmHg without fresh coating. Curve C shows that of runs with the same mixture each performed at the specified temperature after repetition of several runs at 200°C followed by evacuation at the same temperature. Results of curve I, II or C are referred to in what follows as those on the fresh, used or carbided film respectively.

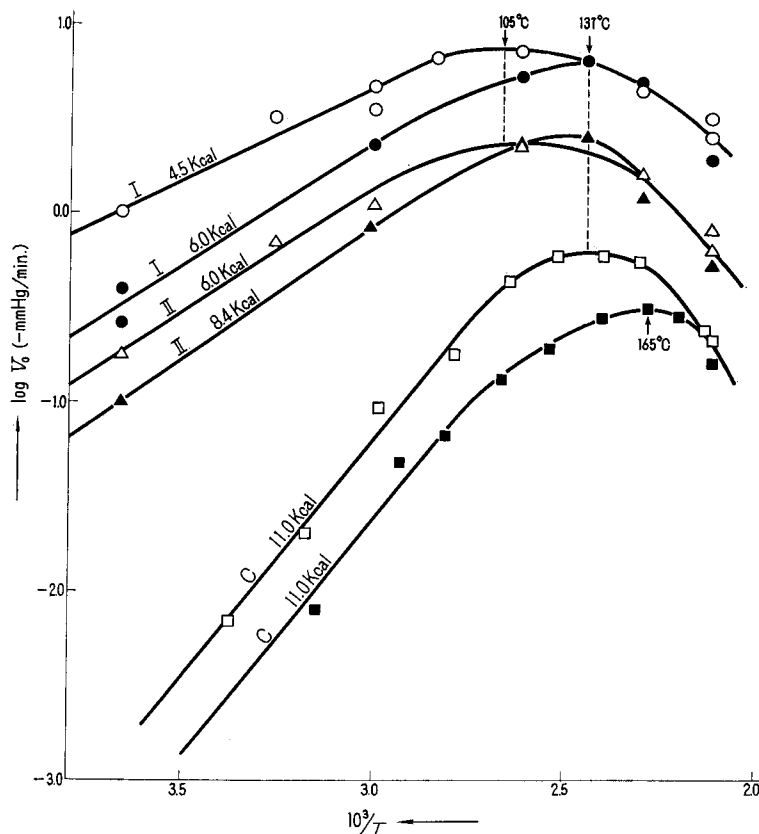


Fig. 1. ARRHENIUS plots of hydrogenation rates by protium ($\circ, \triangle, \square$) and by deuterium ($\bullet, \blacktriangle, \blacksquare$); curve I, II or C is the result on fresh, used or carbided film respectively, with heat of activation and optimum temperature annexed to each.

The heat of activation below the optimum either of protation or deuteration with equimolar mixture of 20 mmHg initial total pressure increased up to a final and very steady value of 11 Kcal by repeating the run with the same

mixture at each temperature followed by evacuation at the same temperature without fresh coating, in accordance with the result obtained by JENKINS and RIDEAL⁹⁾ on a carbided surface; this increase of heat of activation is accompanied by *ca.* 30°C upward shift of the optimum temperature. The optimum temperature of deuteration is higher than that of protation by *ca.* 30°C whether the film is fresh, used or carbided.

Eig. 1 shows that the isotopic effect of hydrogenation rate on fresh film is *ca.* 3.3 and 2.0 at 0°C and 50°C respectively, whereas it is evenly *ca.* 2.2 on carbided film below the optimum temperature. Above the optimum temperature no isotopic effect on hydrogenation rate is perceptible within experimental error on every film.

Deuteration at Temperature Below the Optimum.

Table 1 shows the distributions of deuteroethylenes and deuteroethanes obtained at the earliest stage of the reaction at 0°C on fresh film, where evolved ethane attained an amount sufficient for mass spectrometric analysis, while Table 2 the relative heights of peaks M_2 , M_3 and M_4 of reacted hydrogen in samples gathered up to that stage of run 2 in Table 1.

TABLE 1. Distributions of deuterohydrocarbons formed by deuteration of 10 mmHg light ethylene by deuterium of different initial partial pressures at 0°C.

No. of run	Initial partial pressure of D_2 mmHg	Deuteration %	Relative abundances of deuterohydrocarbons, %											
			Ethylenes				Ethanes							
			E_1	E_2	E_3	E_4	A_0	A_1	A_2	A_3	A_4	A_5	A_6	
2	10	33	13	1	0	0	45	23	18	0	0	0	0	
3	10	45	12	1	0	0	35	28	19	4	1	0	0	
4	43	12	27	3	0	0	40	24	3	2	0	0	0	
5	107	29	29	5	2	0	23	19	13	4	2	1	0	
7	138	36	14	1	0	0	27	10	36	7	2	1	1	

TABLE 2. Mass spectrum of reacted hydrogen gas of run 2 in Table 1.

Deuteration %		0	15	20	27	33
Relative heights of peaks	M_2	4	5	5	7	5
	M_3	2	2	2	2	2
	M_4	94	93	93	91	93

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"Deteration %" both in the Tables shows the percent of decrease of total pressure on the initial partial pressure of ethylene. The column below "Relative abundances of deuterohydrocarbons, %" shows those of monodeuteroethylene E_1 *etc.*, light ethane A_0 and monodeuteroethane A_1 *etc.* by percent of the total hydrocarbon sampled.

Results similar to the above were obtained at 50°C.

Deuteration at 200°C.

Reaction of light ethylene and deuterium both of 10 mmHg initial partial pressures were conducted on fresh film at 200°C, which is sufficiently high above the optimum temperature as seen from Fig. 1; their results are shown in Tables 3 and 4. Table 4 gives the mass spectrum of reacted hydrogen in samples gathered up to that stage of run 12 in Table 3.

TABLE 3. Distributions of deuterohydrocarbons formed by reaction of equimolar mixture of ethylene and deuterium of 20 mmHg initial total pressure at 200°C.

No. of run	Deuteration %	Relative abundances of deuterohydrocarbons, %									
		Ethylenes				Ethanes					
		E_1	E_2	E_3	E_4	A_0	A_1	A_2	A_3	A_4	A_5 A_6
11	20	38	27	13	0	4	6	7	4	2	0 0
12	31	25	25	11	3	3	8	12	7	4	1 0

TABLE 4. Mass spectrum of reacted hydrogen gas of run 12 in Table 3.

Deuteration %		0	13	31
Relative heights of peaks	M_2	11	35	47
	M_3	5	31	27
	M_4	84	34	26

The first column of Table 2 or 4 shows the result of mass spectrometric analysis of the gas sampled immediately after the introduction of the original equimolar mixture into reaction vessel, which is assured free from ethane as shown in the Tables. Considerably high values of M_2 and M_3 in Tables 2 and 4 are interpreted as due to an appreciable decomposition of light ethylene on the fresh surface, which is enhanced at the higher temperature in the latter case.

Discussion

1. Tables 1 and 2 show that at temperatures below the optimum, protium atoms did not practically penetrate from light ethylene into deuterium gas in spite of the remarkable extent of deuteration of ethylene and such formation of ethanes, which verifies the conclusion from the structure theory that the step I_b determines the rate below the optimum temperature. The predominant formation of light ethane confirms the previous results of TURKEVICH *et al.*³⁾, which was theoretically accounted for by KEII²⁾ on the basis of the above theory.

2. The results of Table 1 verifies qualitatively our previous prediction⁴⁾ that dideuteroethane predominates once again below the optimum temperature in place of light ethane in sufficient excess of deuterium, although A_0 then exceeds A_1 as observed not in accordance with the theoretical prediction. This might be due to dissociative adsorption of light ethylene in the initial stage of the reaction on fresh film providing extra protium atom adsorbed, hence too high an amount of light ethane.

3. The present results in Table 3 verifies the prediction of KEII²⁾ that dideuteroethane should predominate at temperatures above the optimum taking place of light ethane below it; relative magnitudes of A_0 and A_1 are here in conformity with the theoretical prediction.

4. The observed isotopic effects on hydrogenation rate and the optimum temperature are now qualitatively interpreted as follows on the basis of the conclusion of the structure theory¹⁾ that the rate-determining step I_b switches over to III at the optimum temperature with rise of temperature.

The initial system of I_b consists practically exclusively of deuterium as shown by the observed results in Table 2 at temperatures below the optimum, where I_b governs the rate according to the structure theory. This accounts for the observed isotopic effect on hydrogenation rate at least qualitatively. MATSUZAKI¹⁰⁾ has concluded, on the other hand, according to the structure theory that the deuterium fraction of adsorbed hydrogen above the optimum temperature, where III governs the rate, does not exceed 0.38 up to 150°C at 10 mmHg partial pressures each of deuterium and ethylene. It follows that the isotopic effect on hydrogenation rate above the optimum may be imperceptible, on account of an appreciable errors of its determination in this region.

The optimum temperature is now according to the structure theory that of the intersection of the two lines of $\mathcal{R}(I_b)$ and $\mathcal{R}(III)$ as shown in Fig. 2, each being the rate of the overall reaction which would be observed if other step than I_b or III respectively were in partial equilibria. Hence the value

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$\mathfrak{R}(I_b)_D$ of $\mathfrak{R}(I_b)$ in case of deuteration should lie lower than that $\mathfrak{R}(I_b)_P$ of $\mathfrak{R}(I_b)$ in case of protation, while the isotopic effect on $\mathfrak{R}(III)$ is practically imperceptible. It follows that the optimum of deuteration should lie at a temperature higher than that of protation.

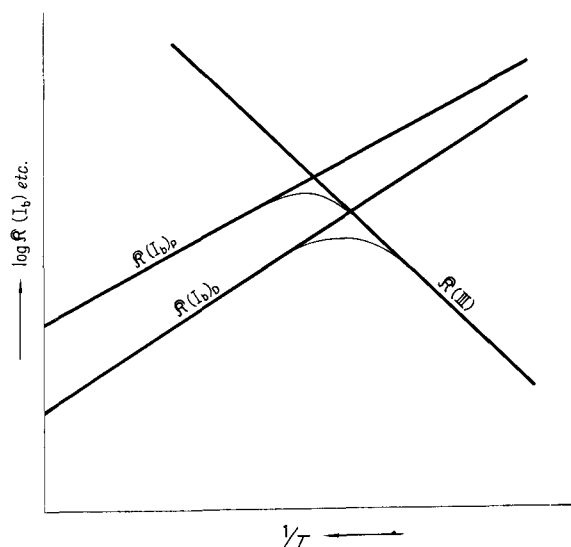


Fig. 2. Isotopic effect on the structure; $\mathfrak{R}(I_b)_D$ or $\mathfrak{R}(I_b)_P$ is $\mathfrak{R}(I_b)$ referred to deuteration or protation respectively.

The optimum temperature on carbided film is higher than that on fresh film, which may be understood similarly that carbon residues on the carbided film retards I_b below the optimum, but does III above the optimum impartially, because of instantaneous carbiding, whether the surface be preliminarily fresh or carbided leaving $\mathfrak{R}(III)$ practically not shifted.

The detailed discussion on the isotopic effect on the retardation by carbon residues will be given in a later paper on the basis of more detailed observations now in progress.

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