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Radiotracer Studies on the Interaction of Hydrogen with Platinum Black Catalysts

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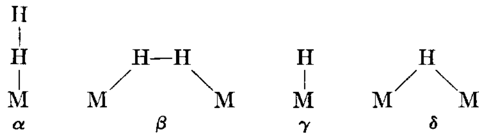
Chemisorption at 360°C of hydrogen labeled with tritium has been studied on unsupported platinum black catalysts, thus avoiding complications from spillover. Catalysts in a microcatalytic reactor were exposed to pulses or to static treatment with H_2/HT. After helium flow over these catalysts tritium could be detected by radiochromatography in subsequent pulses of ethylene, cyclohexene and *n*-hex-1-ene, or H_2 which passed over the catalysts. From the time-dependence of the phenomena and other evidence, it was deduced that H_2/HT in the catalysts was present in positions in the matrix which were accessible or inaccessible to hydrocarbons and hydrogen. Scintillation counting was used to confirm the retention and possible absorption of tritium by the catalysts.

When the nature of the hydrogen chemisorbed on metals is studied by surface potential and electrical conductivity methods, it appears that there is more than one type of adsorbed species (*1–3*). There is controversy over whether it is atomic, molecular or charged. Infrared (*4*) observations can be interpreted in terms of atoms lying on surface platinum atoms and in interstices. These may correspond to Toya's (*5*) theoretical *r*- and *s*-types. Except for the ir work (*4*), which showed chemisorption of hydrogen at 400 Torr and ~350°C, these studies have been made at low temperature (<20°C) and pressure (<1 Torr).

Temperature-programmed desorption (TPD) of hydrogen from platinum black (*6*) between −196 and 400°C revealed four types of chemisorbed species, α, β, γ and δ, with TPD peaks at −100, −20, 90 and 300°C. α-Hydrogen adsorbed only below −100°C and δ-hydrogen only below 50°C. Pressures during adsorption were 1–2 Torr: higher pressure and higher adsorption temperatures (100 to 300°C) led to overlapping γ + δ peaks (*6, 7*). The same sites appeared to account for the β-, γ- and δ-forms. Coverage by β-hydrogen, θ_β, decreased as adsorption time increased, but $(\theta_\beta + \theta_\gamma + \theta_\delta)$ remained constant. Preadsorption of δ-hydrogen lowered θ_β and θ_γ. Tsuchiya, Amenomiya and Cvetanovič (*6*) suggested that the four forms might be:



Thus Toya's *r*-type might be equivalent to γ, his *s*-type to δ.

Chemisorbed hydrogen may participate in catalytic conversions or it may create catalytically active sites. Only α- and γ-hydrogen were active in H_2–D_2 exchange between −76 and −196°C (*8*). Akhtar and Tompkins (*9*) found that hydrogen chemisorbed in a "second layer" was very active in low-temperature hydrogenation (*9*). Exchange of tritium atoms chemisorbed on unsupported platinum or nickel with ethylene and propylene has been studied at 0°C and with methane up to 276°C (*10, 28*). Platinum prepared in different ways

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showed marked differences in activity (*10*).

For hydrocarbon reactions at higher temperatures, hydrogen may be decisive in determining extent and direction of catalysis. When a palladium or nickel thimble was used as catalyst, hydrogen diffusion into the metal accompanied loss of catalytic activity (*11–13*). The presence of gaseous hydrogen can influence product composition when *n*-hexane reacts over platinum black (*14*). Presence of hydrogen may prevent formation of carbonaceous deposits (*11, 15*) or it may create the active centers (*16*). When gas-phase hydrogen is absent it is difficult to know how much hydrogen is on the surface of a catalyst and the extent of its activity in catalysis. Thus carbonaceous residue deposition may displace hydrogen: alternatively lack of hydrogen may induce rupture of C–H bonds to form residues and M–H species.

There are few studies of retention of hydrogen by platinum at elevated temperatures. Radioactive tracers are attractive for such a study: their use has shown (*10*) some retention of tritium on Pt black up to 276°C and that tritium added to supported metal catalysts is partially retained by them on subsequent flushing with helium (*17*). Retained hydrogen can react with hydrocarbons (*18, 19*) and at least some of the retained hydrogen can be detected in this way. Such studies on supported catalysts are complicated by spillover; this migration of hydrogen from metal to support gives rise to apparently high hydrogen to metal ratios (*18, 19*). Spillover hydrogen is believed to be inactive while on the support (*20*) but when hydrogen is removed from the metal, back-migration of hydrogen from the support leads to possible participation in catalysis (*18, 19*). In view of the evidence quoted, spillover need not be the only cause of hydrogen retention by the metal of a catalyst.

We decided to investigate the possibility of retention of tritium-labeled hydrogen on a platinum black catalyst, where complications from spillover onto support were absent. We planned to establish the extent of participation of retained hydrogen in hydrocarbon reactions.

EXPERIMENTAL METHODS

Catalyst. Pt black was prepared by HCHO reduction of H_2PtCl_6 in concentrated KOH (*21*).

Materials. He carrier gas (Air Products Ltd.) was dried by molecular sieve 5A at room temperature; oxygen was removed by Cu at dull red heat and the He finally dried over $Mg(ClO_4)_2$. Cylinder hydrogen purified in an Engelhard Deoxo unit was dried by molecular sieve.

Carrier-free tritium (Radiochemical Centre, Amersham) was diluted with hydrogen from a palladium thimble to an activity of $0.3–1.0 \times 10^6$ cpm/ml, (H:T ratio 10^7:1). Any isotope effect could alter this ratio only to a small extent and was neglected. We refer to this dilute labeled hydrogen as "tritium."

Ethylene (Matheson Research Grade, British Oxygen Co.) was de-aerated by freeze-and-thaw cycles using liquid nitrogen, evacuating to 10^{-3} Torr during freezing; it contained <0.05% ethane and <0.1% N_2. Cyclohexene and *n*-hexene-1 (puriss. grades) were treated with ferrous ammonium sulfate, followed by distillation.

Apparatus. A pulse-type microcatalytic reactor [cf. (*18*)] was coupled to a Beckman GC2 gas chromatograph with thermal conductivity detector. Hydrogen and C_2-hydrocarbons were separated on a 300 cm silica gel column at 56°C, C_6-hydrocarbons on a 100 cm 15% tricresyl phosphate-on-chromosorb column, at 56°C for cyclohexene, at 39°C for *n*-hexene. The carrier gas for catalyst and chromatography was helium, 60 ml/min.

Radioactivity was measured in a 50 ml gas-flow proportional counter connected after the chromatographic column. Methane, 5 ml/min, was admixed to the helium before the counter tube. Pulses from the counter were preamplified, led to a ratemeter which activated a second pen on the recorder of the gas chromatograph. A scaler indicated the number of radioactive counts as the basis of the evaluation of radioactivity; the radiochromatogram was used to check if the scaler counts were due to a radioactive *peak* corresponding to a chromatographic peak. This prevented evaluation of minor increases in the background, or "tailing" from previous peaks, as radioactive peaks.

Standard pretreatment of the platinum black in the reactor consisted of it being heated over 25 to 30 min to 360°C in air, and keeping it in air at 360°C for 30 min; a helium flush of 10 min displaced nitrogen and oxygen, followed by hydrogen flow for 60 min; the carrier gas was then switched to helium and the system was ready for use. The reaction temperature was 360°C.

Tritium, as slugs of 0.5 ml, was introduced into the reactor by a gas-tight Hamilton syringe; minor contamination with air (up to 0.5%) was unavoidable; this caused no detectable effect. Tritium (0.5 ml) corresponded to a hydrogen partial pressure at the maximum of 200 to 300 Torr. In some cases the tritium slug of 0.5 ml was left in the closed catalyst system for some time; assuming equilibration, it corresponded to 30–50 Torr hydrogen pressure.

In other cases pretreatment with tritium (of the same activity as in the pulses) was made in a static system, at ~760 Torr hydrogen.

After tritium pretreatments, pulses of inactive hydrogen and ethylene, cyclohexene and *n*-hexene were introduced into the microcatalytic reactor and the radioactivity of the products was measured. Separate experiments established that neither the apparatus nor the chromatographic columns caused tritium retention and exchange.

RESULTS

a. Experiments with Tritium Injections

When tritium was injected on to the catalyst, its radioactivity appeared as a large peak on the radiochromatogram which showed "tailing" due to slow desorption from the catalyst. The radioactivity background was reached within 10–15 min when no more tritium was leaving the catalyst.

When hydrocarbons were injected the products were radioactive (Tables 1–3). This radioactivity originated from the tritium retained by the catalyst; the situation was similar to that observed with supported catalysts (*18*, *19*). With ethylene as starting material (Table 1), methane, ethane, and the small amount of molecular hydrogen produced, were all radioactive. *n*-Hexene-1 and all its products involving

TABLE 1
ETHYLENE EXCHANGE WITH TRITIUM RETAINED BY Pt BLACK[a]

Injection	Sequence of events	Time lapse after HT pulses (min)	Radioactivity in products (counts)
	Air, 5 ml; H_2 flow, 3 min; HT pulse, 0.5 ml		466,400
	He flow, tritium desorption for 1 min		1500
395	Ethylene, 0.5 ml	5	9500[b]
	Air, 5 ml; H_2 flow 3 min; HT pulse, 0.5 ml		451,500
	He flow, tritium desorption for 3 min		2200
394	Ethylene, 0.5 ml	9	4100
	Air, 5 ml; H_2 flow, 3 min; HT pulse, 0.5 ml		465,000
	He flow, tritium desorption for 7 min		2000
396	Ethylene, 0.5 ml	18	Background

[a] Temp, 360°C; helium flow, 60 ml/min; 0.06 g Pt.

[b] Distribution of radioactivity: H_2, ~ 650 counts; CH_4, ~ 2750 counts; C_2H_6, 4200 counts; C_2H_4, 1900 counts. The radiochromatogram showed two distinct though somewhat overlapping peaks for H_2 and CH_4.

TABLE 2

CYCLOHEXENE EXCHANGE WITH TRITIUM RETAINED BY Pt BLACK[a]

Injection no.	Sequence of events	Time lapse after HT pulses (min)	Radioactivity in products (counts)
	SP; then HT, 0.5 ml		390,000
397	Cyclohexene, 3 μl	4	36,500
	SP; then HT, 0.5 ml		410,000
	He flow, tritium desorption for 1 min		1100
398	Cyclohexene, 3 μl	6	12,700
	SP; then HT, 0.5 ml		425,000
301	Cyclohexene, 3 μl	9	~600
	SP; then HT, 0.5 ml		344,000
	He flow, tritium desorption for 20 min		7500
390	Cyclohexene, 3 μl	40	~300

[a] Temp, 360°C; helium flow, 60 ml/min; 0.06 g Pt; standard pretreatment (SP): air, 5 ml; H_2 flow, 3 min; He flow, 20–30 min.

cracking, hydrogenation, isomerization, dehydrogenation and ring closure (*22*) contained tritium (Table 3).

The amount of radioactivity was strongly dependent on the time elapsing between the tritium and hydrocarbon injection. Since hydrogen passed through reactor and column within 2 min and 2.5–3

TABLE 3

TRITIUM CONTENTS OF PRODUCTS OF *n*-HEXENE-1 TRANSFORMATION ON Pt BLACK[a]

Injection no.	Pretreatment of Pt	Radioactivity of HT pulses (counts)	Time between HT and hexene slug (min)	Products		
				Composition (%)		Radioactivity (counts)
385	Air, 10 ml followed by three slugs HT, each 0.5 ml	722,000	5.5	$<C_6$	4.10	32,000
		809,000		Hexane	12.10	17,100
		707,000		Hexenes	76.30	10,000
				Hexadienes	3.95	3500
				Benzene	3.55	8500
386	None	—	16	$<C_6$	1.5	500
				Hexane	1.05	900
				Hexenes	96.45	Background
				Hexadienes	0.65	
				Benzene	0.35	
387	Air, 10 ml followed by three slugs HT, each 0.5 ml	791,000	27	$<C_6$	4.0	1500
		927,000		Hexane	12.35	1300
		924,000		Hexenes	76.2	
				Hexadienes	3.9	Background
				Benzene	3.55	
388	None	—	38	$<C_6$		Background
				Hexane		
				Hexenes		
				Hexadiene		
				Benzene		

[a] Temp, 360°C; helium flow, 60 ml/min; 0.16 g Pt; *n*-hexene-1, 3 μl.

min were necessary for close approach to the radioactivity background, the first hydrocarbon pulse could be injected 4.5–5 min after the tritium pulse. The somewhat elevated background was taken into consideration.

Tables 1–3 show that the amount of radioactivity taken up by hydrocarbons decreased quickly with time. If the injection was made more than 15 min after the tritium pulse, then the radioactivity in the hydrocarbon was hardly distinguishable from background. The tritium desorbed after a tritium pulse (without hydrocarbon injections) appeared as a tail after the radiochromatogram peak. The tritium in this tail was considerably less than the amount in the hydrocarbons in the initial stages after the tritium slug. This meant that rapid desorption of tritium from the platinum could not be solely responsible for the cessation of tritium–hydrocarbon exchange. A second *n*-hexene-1 pulse injected on to a catalyst (which had lost most of its catalytic activity during the interaction with the first pulse) still contained some radioactivity; thus deactivation was not necessarily accompanied by removal of *all* the tritium from the catalyst.

The different radioactivities picked up by different hydrocarbons could have been due to difference in their interaction with the catalyst, or to differences in the extent of exchange. We therefore performed experiments in which two subsequent pulses introduced consisted of either the same or different hydrocarbons. We used ethylene and cyclohexene. The chromatographic column was bypassed and no product analysis was made.

Table 4 shows that although cyclohexene was more efficient in removing tritium from the catalyst, there was no difference in data obtained with these two hydrocarbons which would have suggested different types of hydrogen accessible for one of the hydrocarbons and inaccessible for the other. The data give confirmation that tritium was present on platinum which had a decreased catalytic activity after a hydrocarbon pulse.

The amount of radioactivity taken by the second pulse was nearly independent of the extent of exchange with the first pulse. Thus the state of the catalyst depended on the spontaneous disappearance of exchangeable tritium rather than on the efficiency of the hydrocarbon in removing tritium from the surface.

When hydrogen pulses were passed over the catalyst pretreated with tritium, similar phenomena were observed. The radioactivity held by the platinum persisted longer; subsequent hydrogen pulses became radioactive to a gradually decreasing extent (Fig. 1). If the *first* pulse of inactive

TABLE 4

CONSECUTIVE ETHYLENE AND CYCLOHEXENE EXCHANGE WITH TRITIUM RETAINED BY Pt BLACK[a]

Injection no.	Treatment and sample introduced	Time elapsed between pulses	Radioactivity (counts)
440	SP; then HT, 0.5 ml	—	353,500
441	Ethylene, 0.5 ml	3.5 min after 440	1400
442	Ethylene, 0.5 ml	3.5 min after 441	350
437	SP; then HT 0.5 ml		363,500
438	Cyclohexene, 3 μl	3.5 min after 437	4300
439	Cyclohexene, 3 μl	3.5 min after 438	400
443	SP; then HT, 0.5 ml		218,000
444	Ethylene, 0.5 ml	3.5 min after 443	550
445	Cyclohexene, 3 μl	3.5 min after 444	350
449	SP; then HT, 0.5 ml		213,000
450	Cyclohexene, 3 μl	3.5 min after 449	2600
451	Ethylene, 0.5 ml	3.5 min after 450	Approx 200

[a] Temp, 360°C; helium flow, 60 ml/min; 0.06 g Pt; standard pretreatment (SP): air, 10 ml; H_2 flow, 6–7 min; He flow, 25 min.

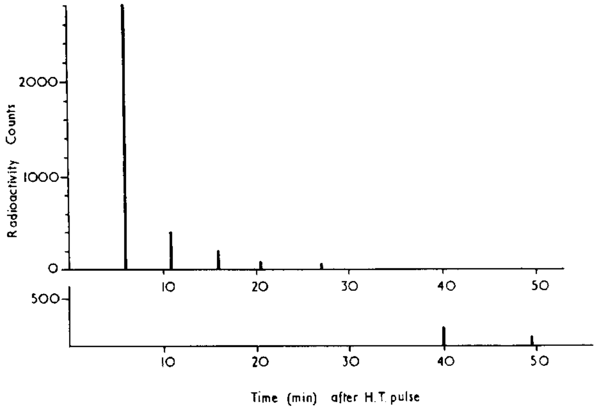

FIG. 1. Interaction of inactive hydrogen pulses with platinum black catalyst (0.06 g) tritiated with slugs. Pretreatment: upper graph: 3 × 0.5 ml tritium, with the total radioactivity of 597,500 counts; lower graph: 0.5 ml tritium, 269,300 counts. The height of the ordinates proportional to the radioactivity of hydrogen pulses (0.5 ml) injected after the tritium slug, in intervals shown on the abscissa. Temp, 360°C.

hydrogen was injected after 40 min, when no radioactivity would have been expected in hydrocarbons, the hydrogen still contained radioactivity (Fig. 1). This confirms that the disappearance of radioactivity in hydrocarbon slugs after about 15 min did not necessarily mean the removal of the hydrogen from the surface: the hydrogen must have migrated to positions inaccessible for hydrocarbons, but accessible for hydrogen.

TABLE 5
HYDROGEN–TRITIUM EXCHANGE ON USED Pt BLACK: INITIAL TRITIUM UPTAKE IN FLOW SYSTEM[a]

Injection no.	Sample (ml)	Time elapsed between injections (min)	Radioactivity (counts)
452	HT, 3 × 0.5		152,000 259,000 488,700
453	H_2, 0.5	6	3200
454	H_2, 0.5	5	1450
455	H_2, 0.5	5	800
456	H_2, 0.5	5	500
457	H_2, 0.5 air, 1	4.5	300
458	H_2, 0.5	4 min after air	150

[a] Temp, 360°C; He Flow, 60 ml/min; 0.06 g Pt; catalyst pretreatment: H_2 and HT slugs, 12 × 0.5 ml C_2H_4, 6 × 3 μl C_6H_{10}, air at 360°C 2 hr, H_2 flow at 360°C, 1 hr.

The repeated use of a Pt black for hydrocarbon reactions and its regeneration with air and hydrogen did not affect its activity for exchange of tritium with subsequent hydrogen pulses: the data from a much-used catalyst (Table 5) resemble closely those in Fig. 1.

b. *Experiments with Static Tritium Treatment of Hydrogen-Pretreated Catalysts*

The phenomena described in Sect. (a) could be enhanced if the contact time was increased by injecting tritium into a closed reactor and maintaining it there for some time (Table 6, cf. Table 5).

Table 7 shows that tritium kept on the hydrogen-pretreated platinum for 1 hr caused an ethylene pulse, added 40 min after tritium release, to be slightly radioactive: this was not so for tritium slugs, cf. Table 1. On the other hand *removal* of tritium held by the catalyst was more efficient when inactive hydrogen was kept in contact with it for some time. Table 7 shows that hydrogen pulses, added to the catalyst after ethylene, could pick up considerable radioactivity; in confirmation of the results in Table 5, air could not remove tritium from the catalyst, although it reduced the amount exchangeable with the next hydrogen pulse. Water from the surface $H_2 + O_2$ reaction was adsorbed on the

TABLE 6
Hydrogen–Tritium Exchange on Pt Black: Initial Tritium Uptake in a Static System[a]

Injection no.	Sample (ml)	Time elapsed between two injections (min)	Radioactivity (counts)
325	HT, 0.5, kept on the Pt for 5 min	—	260,000
326	H_2, 0.5	5 min after release of 325	31,300
327	H_2, 0.5	4	3600
328	H_2, 0.5	4	1500
329	H_2, 0.5	4	800
330	H_2, 0.5	5	540

[a] Temp, 360°C; He flow, 60 ml/min; 0.06 g Pt; pretreatment: heating to 360°C in air, kept for 30 min, then H_2 flow for 60 min at 360°C, then He flow for 120 min.

silica gel column and did not reach the radioactivity detector.

c. *Experiments with a Catalyst Prepared and Pretreated with Tritiated Hydrogen*

Experiments in (a) and (b) were made with platinum black prepared and pretreated with inactive hydrogen. One might suspect that interactions occurred between tritium retained by the catalyst and "primary" hydrogen taken up during pretreatment, leading to dilution of the former and a fall in observed counts (see Tables 5 and 6). Investigations were completed in experiments where the "primary" hydrogen in contact with the platinum was radioactive. This might result in an addition of tritium from the catalyst to H_2 pulses, maintaining HT count rates at a rising or constant level. Table 8 shows that the first pulse acquired activity from the tritium which had not desorbed. The radioactivity of subsequent H_2 pulses reached a constant level if they were introduced in equal time

TABLE 7
Removal of Tritium from Pt Black by Ethylene Then Hydrogen[a]

Injection no.	Catalyst treatment and sample	Time elapsed (min)	Radioactivity (counts)
—	Air, 2 × 10 ml; H_2 flow, 6 min; He flow, 10 min; then HT, 1 ml maintained over Pt for 60 min		
	He flow into counter	0	760,000
	He flow into counter HT desorption	23.5	6800
429	Ethylene, 0.5 ml	40	~300
430	H_2, 0.5 ml	50	630
431	H_2, 1 ml, maintained over Pt for 20 min		
	He flow into counter	0	3900
432	H_2, 1 ml, maintained over Pt for 60 min		
	He flow into counter	0	2400
	air, 5 ml, pulse		—
433	H_2, 0.5 ml	5.5 min after air	550
434	H_2, 1 ml, maintained over Pt for 20 min		
	He flow into counter	0	2650

[a] Temp, 360°C; He flow, 60 ml/min; 0.06 g Pt.

TABLE 8

HYDROGEN TRITIUM EXCHANGE ON PLATINUM BLACK[a]

Injection no.		Sample (ml)	Time elapsed between injections (min)	Radioactivity (counts)
484	1	H_2, 0.5	5 min after release of HT	~10,000
485	2	H_2, 0.5	66	1100
486	3	H_2, 0.5	4.5	550
487	4	H_2, 0.5	4.5	510
488	5	H_2, 0.5	20	640
489	6	H_2, 0.5	4.5	460
490	7	H_2, 0.5	Kept for 20 min on the catalyst	2340
491	8	H_2, 0.5	5	530
492	9	H_2, 0.5	4	320
493	10	H_2, 0.5	10	450
494		Ethylene, 0.5	5	~200
495		H_2, 0.5 air, 1	10	360
496		H_2, 0.5	5 min after air	140
497		H_2, 0.5	6.5	300
498		H_2, 0.5	4	260

[a] Pt exposed to HT at 730 Torr for 75 min; Temp, 360°C; He flow, 60 ml/min; 0.06 g Pt; pretreatment: catalyst heated in air to 130°C, then in He to 360°C: HT 730 Torr for 75 min; activity: 0.5 ml HT ≡ 163,200 counts.

intervals. When this interval was long, pulse 488, the radioactivity of the pulse increased, showing that the specific radioactivity of the surface layer was determined by interaction of gas-phase inactive hydrogen (from the previous pulse) and radioactive primary tritium. Introduction of H_2 pulses necessarily diluted the surface layer, but lapse of time allowed the primary tritium to come again to the surface.

The same was true when hydrogen was kept on the catalyst' pulse 490. Pulse 491 met a surface layer corresponding to the higher radioactivity of 490, but it diluted the surface hydrogen for 492. The effect was most marked when a hydrogen flow (at about 1 atm) was applied (Fig. 2): the first H_2 pulse after the H_2 flow met a surface layer rich in ^1H and was almost nonradioactive. The effect of air was the same as before.

The radioactivity taken up with ethylene Table 8, was hardly higher than background. Cyclohexene took up slightly

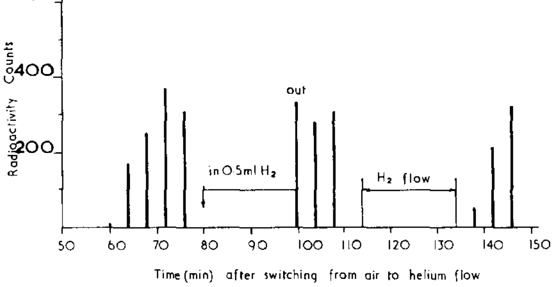

FIG. 2. Reappearance of radioactivity in hydrogen pulses introduced after air and hydrogen treatment. 0.06 g catalyst was pretreated with tritium, then exposed to air (1 atm). The graph shows the radioactivity taken up by 0.5 ml slugs of hydrogen introduced into He flow after this and a subsequent hydrogen flow (1 atm) treatment at the intervals shown. Temp, 360°C.

TABLE 9
ETHYLENE AND CYCLOHEXENE EXCHANGE WITH TRITIUM RETAINED BY Pt BLACK[a]

Injection no.	Catalyst treatment and sample	Time elapsed	Radioactivity (counts)
500	Air, 5 ml, H_2 flow 6 min ethylene, 0.5 ml	2 min after H_2	Background
499	Air, 5 ml, H_2 flow 6 min ethylene, 0.5 ml	60 min after H_2	~180[b]
501	Air, 5 ml, H_2 flow 6 min cyclohexene, 3 μl	3 min after H_2	~130
502	Air, 5 ml, H_2 flow 6 min cyclohexene, 3 μl	40 min after H_2	320
503	1 ml air only cyclohexene, 3 μl	2.5 min after air	~280

[a] Pt exposed to HT at 730 Torr for 75 min (see Table 8). Temp, 360°C; He flow, 60 ml/min; 0.06 g Pt.
[b] No distinct peaks, just higher than normal background.

higher radioactivity, and demonstrated the same phenomenon as for added inactive hydrogen pulses (Table 9).

d. Direct Measurement of Tritium Held by the Platinum Black

Since repeated hydrogen pulses did not exhaust the tritium associated with the catalyst (Table 6), we decided to attempt a direct observation of retained tritium. Pt black samples were immersed in a liquid scintillator and their radioactivity was measured by scintillation counting (*23*). Catalysts examined after the experiments in Tables 5, 8, and 9 contained easily measurable amounts of tritium. Table 10 shows a compilation of treatments and resulting radioactivities. The experiments involved exposure of the platinum black to air at room temperature; air evidently did not remove this tritium from the platinum. Hydrogen treatment of about 24 hr removed all the tritium, even though it had been taken up during the primary treatment.

TABLE 10
MEASUREMENT OF THE RADIOACTIVITY OF TRITIATED PLATINUM CATALYSTS BY A LIQUID SCINTILLATION COUNTING METHOD

Catalyst	Radioactivity (cpm/mg Pt)
Sample after treatment in Table 5	1125
Sample after treatment in Tables 8 and 9	385
Same, H_2 flow at 360°C for 24 hr 1 atm	0

DISCUSSION

In catalytic conversions and exchange processes hydrogen has been regarded as a surface species. Excess uptakes of hydrogen by supported metals have been accounted for by overspill onto supports (*18–20*).

Our experiments show that the situation is more complex. They showed that there was hydrogen retained by platinum black catalysts at 360°C, long after the initial contact with gaseous hydrogen ended. Detection of this hydrogen was by exchange between tritium and hydrogen and between tritium and hydrocarbons during their catalytic reactions and direct scintillation counting of retained tritium.

Exchange took place between tritium, in preadsorbed states, and molecules arriving from the gas phase: this proved to be a successful way of establishing the presence and properties of the tritium retained by the catalysts. Exchange is rapid compared with other hydrocarbon transformations and we consider it an efficient process for indicating surface radioactivity [cf. (*24*)].

After a catalyst had been exposed to a tritium pulse, large amounts of tritium appeared in the products from injected pulses of hydrocarbons. The radioactivity of the products decreased rapidly to almost nothing when time elapsed between the initial tritium injection and that of the hydrocarbon. Yet, in flowing helium, tritium was not being desorbed to account for the lack of tritium in the hydrocarbons. We consider it significant that even after hydrocarbons passed over the catalyst and no radioactivity appeared in the products, it was possible to detect retained tritium by exchange with pulses of hydrogen. This process was not inhibited by carbonaceous residues present on the catalysts (*25*).

The time during which tritium became inaccessible to hydrocarbon exchange was between 10 and 50 min at 360°C and depended on the initial uptake of radioactivity, Tables 1 and 8, and the efficiency of the hydrocarbon in finding the tritium on the metal, Tables 1 and 3. A striking result was that a catalyst could be exposed to tritium which became temporarily unavailable for hydrogen exchange, yet it was possible, Table 8 and Fig. 2, to bring about the reappearance of this tritium.

These results can be explained if we assume *two types* of adsorbed hydrogen on the surface. On introducing a tritium pulse to platinum black at 360°C it generated a "hydrocarbon-accessible" hydrogen region (I) on the surface. Some of the radioactive hydrogen desorbed from this layer, as the tailing of the radiochromatogram indicated, but a larger fraction must have migrated to another "hydrogen-accessible and hydrocarbon-inaccessible" region (II). This could not be removed by oxygen, but could be detected by scintillation counting and it supplied the species which reappeared to take part in exchange. It appears that these two types of hydrogen could transform into each other. Some of the hydrogen taken up would be retained for long periods after the contact between platinum and gaseous hydrogen has ceased. Thus pretreatment of Pt black involves uptake of a "primary" form of hydrogen. This idea was explored in the section on *preparation and pretreatment* of catalysts in tritium. The results in Table 8 and Fig. 2 showed that this primary hydrogen can reappear. Retention of hydrogen or tritium could take place through exchange between the hydrogen of the catalyst, and gaseous hydrogen. The longer the time that was allowed, the greater was the extent of exchange, Table 7.

We shall designate hydrogen adsorbed on Pt black from the gas as type HaI and enquire whether it is an intermediate which disappears during the lapse of a few minutes after a hydrogen pulse. Thus hydrogen could be adsorbed on sites where it might interact with hydrocarbon, but could also migrate to other sites where this interaction was impossible, leaving empty sites. The role of hydrogen is important, for extensive hydrogen chemisorption can decrease the extent of hydrocarbon conversion by displacing it from a surface (*14*).

We reject the idea that sites previously occupied by hydrogen became empty. Table 3 shows that there was no difference between the catalytic activities of platinum black 5 and 27 min after a tritium pulse: thus hydrogen concentration on active sites must have been similar in both cases: in the first case this hydrogen was radioactive, in the second case, nonradioactive.

During the period after a tritium pulse a *minor* desorption occurred and there was a redistribution of hydrogen between HaI sites and another type, viz, HaII. Thus radioactive atoms would be distributed between the two forms to give a uniform specific activity in HaI and HaII. Tritium arriving from the gas phase would thereby have its specific activity reduced: the opposite would occur when hydrogen arrived from the gas phase. The marked falls observed in exchangeable radioactivity suggests that HaII is more extensive than HaI.

These ideas are supported by the observation that when retained species were equilibrated and the overall radioactivity of the catalyst was high, the hydrocarbon products could be only slightly radioactive. In other cases, Table 1, the hydrocarbon activity fell to background levels.

The fact that tritium retained by the catalyst moved from a hydrocarbon-accessible position to a hydrocarbon-inaccessible position does not imply that there was no *hydrogen* in the hydrocarbon-accessible sites. Just as hydrocarbon reacted with HaI species, oxygen interacted only with HaI and was able to replace or displace it: it could not remove HaII. The accumulation of carbonaceous deposits on the surface involved replacement of some of the surface hydrogen (Table 1): this affected only HaI.

Hydrogen from the gas phase adsorbed into the form HaI which began its interaction with HaII. If sufficient time were allowed, all the hydrogen participated in exchange with the gas phase (Table 10).

All the facts could be consistently interpreted on the basis of the reaction scheme:

$$H_2(g) \rightleftarrows \mathrm{HaI} \rightleftarrows \mathrm{HaII}. \quad (1)$$

Radioactivity picked up by the hydrogen or hydrocarbon pulses was dependent on the immediate past history of the catalyst (i.e., upon the fate of HaI). This was also true when the primary hydrogen, which determined the specific radioactivity of HaII, was radioactive.

The decrease in exchange between gas-phase hydrogen and adsorbed species on an oxygenated surface also supports this scheme, since replacement of HaI with oxygen rendered HaII temporarily inaccessible. We have no proof of the existence of a direct interaction between $H_2(g)$ and HaII; if such a reaction took place it evidently had minor importance compared with those in Eq. (1).

It is difficult to decide which of the chemisorbed species suggested in the literature can be identified with HaI and HaII. The intermediate HaI might be a chemisorbed molecule which transforms into chemisorbed atoms but it would be difficult to claim a reasonable lifetime for chemisorbed hydrogen molecules at the temperature of the experiments.

There is the possibility that our two species are hydrogen atoms chemisorbed in different ways: HaI could correspond to Toya's r-type (*5*) and Cvetanovic's γ-type (*6*), while HaII to the s-type and δ-type, respectively: this would be in agreement with the "accessibility" phenomena. There is one contradiction; the thermal desorption experiments showed the desorption peak of the γ- and δ-hydrogen at 90 and 300°C, respectively. These species would not be expected to be stable at 360°C.

In thermal desorption at 10^{-5} Torr it may be easier for chemisorbed molecules to leave the catalyst than in the case of removal of hydrogen by helium at 1 atm. On the other hand, thermal desorption is not able to detect what is left on the catalyst: a remaining, fifth, type of hydrogen on the platinum black is not in contradiction with the experiments of Tsuchiya, Amenomiya and Cvetanovic (*6*).

Lang, Joyner and Somorjai (*26*) elegantly showed the relative ease of hydrogen *absorption* on stepped high index surfaces of platinum single crystals: these structures may be the active sites on dispersed metals. Their absorbed hydrogen disappeared on heating the crystal in vacuum: on oxygen treatment it reappeared at somewhat lower temperature. This cycle could be repeated several times.

This shows striking resemblances to some of our findings, e.g., tritium found in the liquid scintillator experiments. Hydrogen may penetrate into inner layers of the platinum black catalyst, since during pretreatment of the catalyst with hydrogen, marked sintering involving severe recrystallization and tenfold decrease of specific surface takes place (*27*), which may facilitate the incorporation of hydrogen. We assume that HaII may be *absorbed* hydrogen which interacts with the gas phase by migrating to the surface to form an adsorbed layer. Absorption would explain why HaII was larger than HaI.

Since *all* the hydrogen taken up in the primary preparation process could be exchanged, either there was no *absorbed* hydrogen present, or if there was, it must have been interconvertible with *adsorbed* hydrogen.

HaI does not correspond to the γ- and δ-type hydrogens: it probably includes both. When Tsuchiya, Amenomiya and Cvetanovic (*6*) and Komers, Amenomiya and Cvetanovic (*7*) studied adsorption at higher (50–100 Torr) pressures, they found only one desorption peak, an overlapping γ- and δ-peak. In this case, which is near to our condition, it is likely that large concentrations of hydrogen generated both chemisorbed types; these could transform into each other and eventually into absorbed hydrogen. Hydrogen chemisorbed interstitially may be regarded as the "surface layer" of a bulk absorbed hydrogen, the matrix of which is superposed on to the matrix of the platinum crystal. Dissolved hydrogen may be concentrated near the surface (*26*), giving rise to a "chemisorbed layer" of high coverage with a fall in concentration into the bulk of the metal.

Pt black samples with larger crystallites retained more tritium for exchange with ethylene at 0°C (*10*), and this adds additional evidence on the importance of absorption. The extent of the phenomena for our ∼400 Å crystallites might be different with Pt black pretreated to give different crystallite sizes (*29*).

Spillover is not the only phenomenon which can explain hydrogen retention on metal catalysts. It is possible that both absorption and spillover could occur simultaneously. Dispersed platinum on a support which has little "bulk metal" for absorption may favor spillover: absorption may be dominant with unsupported metal.

Barron and co-workers (*30*) found a peculiar variation in selectivity of hydrocarbon isomerization on supported platinum: on very finely dispersed platinum only C_5-cyclization and subsequent ring opening took place, while on platinum with larger particles both this and bond-shift isomerization occurred. Prevalence of these mechanisms on a platinum black catalyst has also been found to depend on the amount of hydrogen in the gas phase (*16*). It can be assumed that dispersion effects may be connected with different ways of hydrogen disposal on the catalyst: spillover may provide a hydrogen-rich environment with finely dispersed platinum. This concept needs further experimental verification.

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