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Regioselective Isotopic Exchange between Propane and Deuterium over Illuminated Pt/TiO$_2$ Catalyst below Room Temperature

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Propane–deuterium isotopic exchange over an illuminated (300–410 nm) 0.5 wt% Pt/TiO$_2$ (anatase) catalyst was carried out at 263 K with a C_3H_8/D_2 ratio of 1/15. An initial selectivity of 100% in monodeuteropropane was found with a nonoptimized quantum yield of ca. 0.01. By analogy with previous studies dealing with cyclopentane instead of propane, the photocatalytic mechanism is based on the activation of the deuteroxyl OD$^-$ groups of titania, which are neutralized by the photoproduced holes and subsequently react with weakly adsorbed propane molecules, thus exchanging one hydrogen atom per period of adsorption. The monoexchange concerned predominantly the primary hydrogen atoms. Long-duration experiments, performed in a static photoreactor, indicated that the secondary H atoms exhibit, under these conditions, a much slower exchange rate, which induces the regioselectivity. © 1987 Academic Press, Inc.

INTRODUCTION

For many years, deuterium–alkane isotopic exchange has been used as a test reaction in the study of the reactivities of CH bonds in hydrocarbons and of the nature of the active sites. Pure oxides, such as chromia (*1–3*), alumina (*4, 5*), or titania (*6*), or supported metal catalysts (*7–11*) have thus been investigated. Whereas oxide catalysts generally produce mostly monoexchanged molecules at the beginning of the isotopic exchange (*1, 2, 6, 12*), metal catalysts yield multiply exchanged molecules including perdeuterated molecules. This reaction appears to be a discrimating means for elucidating the reaction mechanism occuring on a bifunctional photocatalyst formed from a metal deposited on a photosensitive support illuminated with wavelengths of energies higher than or equal to its band gap energy. Such a system was studied for cyclopentane–deuterium isotopic exchange (CDIE) on Pt or Ni/TiO$_2$ (*13, 14*). However, all the hydrogen atoms of cyclopentane are equivalent (*4*), so a photocatalytic study of propane with D$_2$ was undertaken in order to (i) confirm the existence of a 100% initial selectivity for monodeuteration observed for CDIE and (ii) investigate a possible difference in reactivity of the primary and secondary hydrogen atoms, leading to regioselectivity.

EXPERIMENTAL

1. *Apparatus*

The propane–deuterium isotopic exchange (PDIE) was carried out in a fixed-bed photoreactor identical to that described in Refs. (*13, 14*), which was connected to a Datametrics Barocel pressure sensor and to a quadrupole analyzer (Riber QMM 17). Illumination was provided by a Philips HPK 125-W lamp through a water-circulating cuvette closed by a 300- to 410-nm filter (Corning 7.60), whose transmittance is centered on the most intense Hg band at 365 nm. A mean radiant flux of 4 mW cm^{-2} reached the catalyst layer.

2. *Catalyst*

The catalyst contained 0.5 wt% Pt deposited on TiO$_2$ (P-25 Degussa, 50 m^2 g^{-1}, mainly anatase). This Pt weight percentage was chosen because it corresponds to an

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optimum found for CDIE (*14*) as well as for other photocatalytic reactions such as the dehydrogenation of alcohols (*15*). This sample was prepared by the impregnation method. A suspension of TiO_2 in H_2PtCl_6 solution was evacuated at 353 K in a rotating flask and dried at 383 K for 15 h. The resulting solid was calcined at 400°C in flowing oxygen for 2 h, reduced in flowing hydrogen at 753 K for 15 h, and cooled in a nitrogen flow before storage at room temperature. TEM shows homodispersed crystallites with a mean diameter of 2 nm (*15*).

3. *Procedure*

For each PDIE experiment, a photocatalyst layer was uniformly deposited on the bottom window of the reactor from a slurry containing 100 mg of the Pt/TiO_2 sample in 4 cm^3 distilled water. It absorbed more than 95% of the incident radiant flux instead of ca. 70% in the case of a mere spreading of the same amount of powder. The pretreatment included the following successive steps: outgassing at room temperature, reduction in 13.3 kPaD_2 (Société Air Liquide, isotopic purity 99.4%) at 573 K for 1 h, evacuation at the same temperature for 1 h before cooling to 263 K (reactor immersed in a bath thermoregulated with a HS40 Huber cryostat). The reaction temperature was such that no exchange could be detected in the dark. Conversely, it was high enough to be independent of HD desorption as the rate-limiting step of the process (*14*). The metal surface was then covered with a small amount of deuterium (13.33 Pa) before the introduction of the reacting mixture (total pressure: 2.13 kPa), which contained a high excess of deuterium (molar ratio $D_2/C_3H_8 = 15$) in order to limit (i) the isotopic dilution resulting from the light hydrogen molecules (HD or H_2) produced by the reaction and (ii) the formation of carbonaceous deposits on the metal (*7*). The mass spectra (ionization voltage 70 V) were corrected for natural ^{13}C content and for fragmentation.

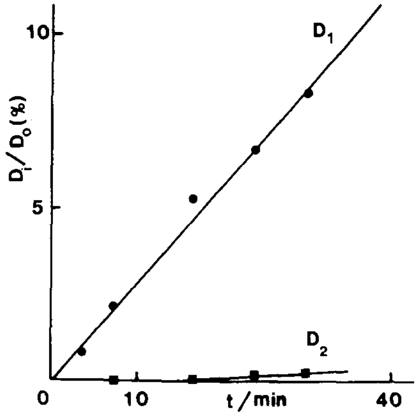


FIG. 1. Kinetics of D_1 formation (D_1/D_0 in percent) over Pt/TiO_2 illuminated at −10°C.

RESULTS

The different $C_3H_{8-i}D_i$ exchanged molecules are denoted D_i throughout the text.

1. *Initial Catalytic Activity and Selectivity*

As soon as the catalytic fixed bed was illuminated, the exchange of propane to D_1 species began. No $C_3H_6D_2$ could be detected within several minutes of UV illumination (Fig. 1). Also, no dehydrogenation products (such as propene) were found, in contrast to the data reported for the exchange catalyzed by TiO_2 at high temperature (*6*). Figure 1 shows that the reaction rate was constant. Extrapolation to time zero indicates an initial 100% selectivity for D_1.

The initial differential quantum yield, defined as the ratio of the reaction rate (in molecules s^{-1}) to the incident flux of efficient photons (in photons s^{-1}) was ca. 0.01, comparable to that obtained for CDIE (*13*). This value corresponded to the experimental conditions used and we did not try to optimize it. No photochemical isotopic exchange—i.e., in absence of catalyst—was detected, in agreement with the nonabsorption of propane in the wavelength range used. In the absence of deposited platinum, an isotopic exchange producing D_1 molecules was also observed but its rate was initially smaller and tended to zero

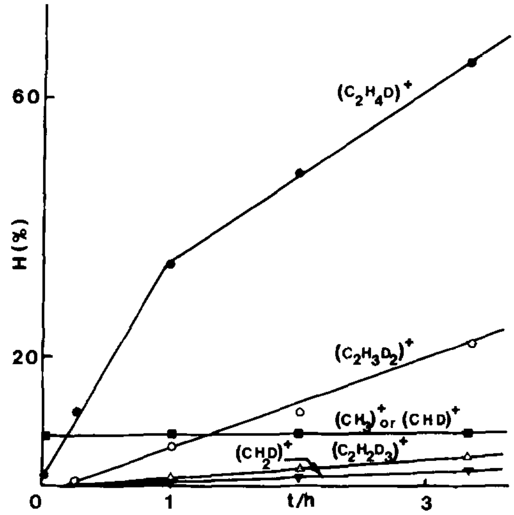


FIG. 2. Kinetics of variations of various fragments of propane on Pt/TiO_2 illuminated at −10°C. The relative peak heights H (%) are calibrated against the base peak at $m/e = 29$.

within about 1 h under our conditions. In other words, this exchange is not photocatalytic without platinum.

This corroborates the results obtained during the study of CDIE (*13*). In this latter case, additional experiments proved the role played by the OD surface groups of TiO_2 as emphasized under Discussion.

2. *Regioselectivity*

Information on the location of the deuterium atom in propane was derived from the kinetics of variations of the concentrations of the various fragments. Fragmentation occurs via the cleavage of either only one C–C bond or of both C–C bonds. In the first case, one gets two fragments $(C_2H_5)^+$ and $(CH3)^+$ at mass 29 and at mass 15, respectively. The second process yields a fragment $(CH_2)^+$ at mass 14 in addition to fragments at mass 15. If D_1 formation occurs with primary H atoms, only the peaks at masses 16 and 30 will increase. If only secondary H atoms are exchanged, the peaks at mass 15 and 30 will increase. Figure 2 shows that the peaks at $m/e = 16$ and 30 increase, whereas the mass-15 peak, which includes $(CH_3)^+$ and $(CHD)^+$ fragments, remains constant. The mass-15 peak remains constant even if peaks at $m/e = 31$ and 32, representing D_2 and D_3 species, are present and increase. Although some H/D redistributions can sometimes occur during the MS ionization process at 70 eV, the fact that only one fragment does not vary with time seems indicative of a preferential exchange of H primary atoms at least until D_3 formation.

3. *Prolonged Isotopic Exchange*

To investigate the difference in reactivity of primary and secondary hydrogen atoms (regioselectivity), long-duration experiments were carried out. Complications in the treatment of the results because of the isotopic dilution of deuterium by the HD or H_2 molecules produced were avoided. For this purpose, besides the use of a large initial excess of D_2 ($D_2/C_3H_8 = 15$), the gaseous phase was regularly and selectively renewed by evacuating the reactor after switching off the illumination, trapping the propane molecules in a cold finger at liquid nitrogen temperature and then admitting a new dose of D_2. This procedure did not perturb the kinetics; the reaction stops immediately in the dark after the illumination has ceased.

Figure 3 shows the isotopic distributions obtained. The formation of D_7 and D_8 demonstrates the reactivity of all H atoms. The relative reactivities of primary and secondary H atoms is discussed in the following section.

4. *Test-Reaction with a Mixture of C_3H_8 and C_3D_8*

A reaction was performed with lightweight propane and perdeuterated propane in the presence or absence of deuterium on illuminated Pt/TiO_2 in order to check the possible existence of a redistribution of H and D atoms, as was observed for benzene molecules over alumina (*5*). PDIE proceeded with the formation of D_1 at a rate close to that observed with the propane–deuterium mixture, while D_8 concentration remained constant and no D_7 was detected.

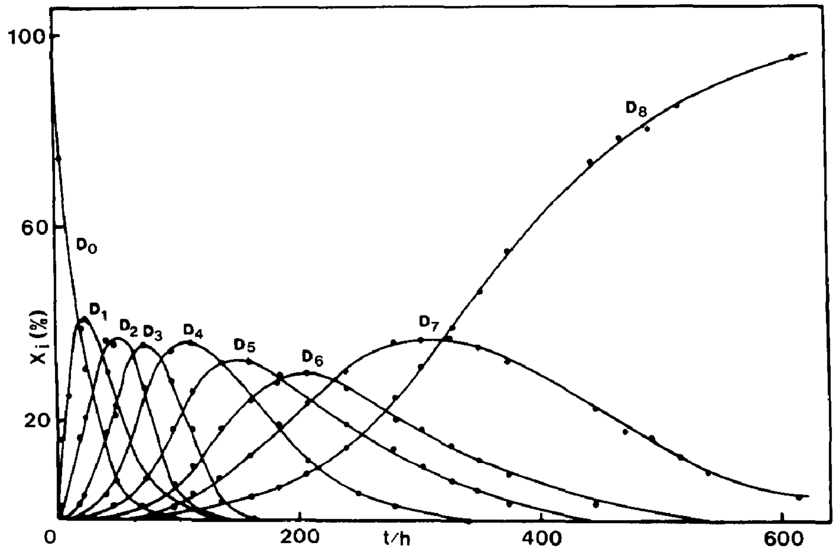


FIG. 3. Kinetic patterns of isotopic distribution for extensive reaction at −10°C (molar fraction x in percent).

DISCUSSION

1. Reaction Mechanism and Catalytic Nature of PDIE

Although the bare support is able to exchange C_3H_8 with D_2 under illumination, the presence of a metal is required to render the reaction photocatalytic, i.e., with a constant rate and with conversions much higher than the limit found for bare titania.

Taking into account its similarities with cyclopentane–deuterium isotopic exchange, we propose for PDIE the reaction steps illustrated in Fig. 4:

Dissociative chemisorption of deuterium on platinum (step 1).

$$D_2 + 2Pt_s \rightleftarrows 2Pt_s - D \qquad (1)$$

Physisorption or weak chemisorption of propane on titania (step 1).

$$C_3H_8(g) \rightleftarrows C_3H_8(ads) \qquad (2)$$

Absorption of light by titania and creation of electron-hole pairs (step 2).

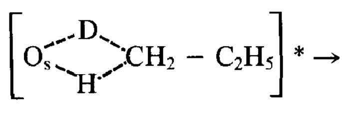
$$h\nu \xrightarrow{(TiO_2)} e^- + p^+ \qquad (3)$$

Reaction of holes with OD_s^- groups, yielding neutral activated OD_s^* radicals, whereas electrons are attracted by Pt particles as observed by photoconductivity (step 3).

$$p^+ + OD_s^- \rightarrow OD_s^* \qquad (4)$$

Deactivation of OD_s^* groups by reaction with adsorbed hydrocarbon molecules (step 4) and formation of activated complexes (step 5) which decompose into D_1 molecules (step 6). Such an associative mechanism for isotopic exchange has previously been proposed (*12, 16*).

$$OD_s^* + C_3H_8(ads) \rightarrow$$



$$\left[O_s \overset{D}{\underset{H}{\lozenge}} CH_2 - C_2H_5 \right]^* \rightarrow$$

$$OH_s + C_3H_7D(g) \qquad (5)$$

Regeneration of OD_s^- groups, which occurs via several steps. The hydroxyl group recovers a negative charge and exchanges with a deuterium atom spilled over the surface of titania, while the light hydrogen atom (proton) migrates toward a platinum particle by reverse spillover (step 7).

$$OH_s + Pt_s - D + e^- \rightarrow$$
$$OD_s^- + Pt_s - H \qquad (6)$$

Desorption of H-containing molecules (step 8).

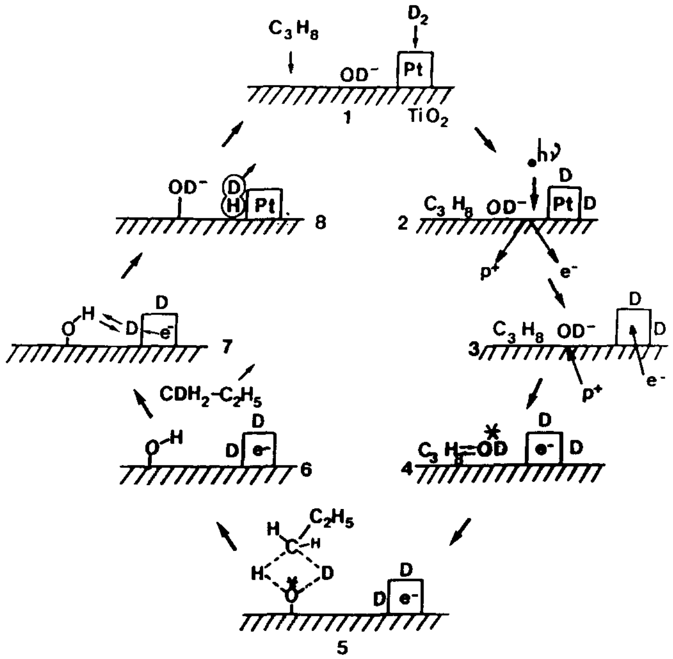


FIG. 4. Photocatalytic cycle for C_3H_8–D_2 isotopic exchange over Pt/TiO_2.

$$Pt_s - H + Pt_s - D \rightarrow 2Pt_s - HD(g) \quad (7)$$

The role of the metal crystallites in the separation and the recombination of electrons and holes has previously been discussed (*14, 15, 17, 18*). The above mechanism accounts for the real catalytic nature of the reaction.

High conversions under a static regime can be obtained—up to the perdeuteration of the propane molecules—during long-duration experiments without apparent deactivation of the catalyst (Fig. 3). Considering that the initial OD^- groups of TiO_2 without Pt deposits are exhausted within 1 h under the same conditions, one can conclude that more than 600 catalytic cycles identical to that described in Fig. 4 can take place on the same active site without significant decline in activity. This absence of deactivation for at least 600 h is also an indication of the catalytic role of the support since otherwise, in the case of a metal activity, a poisoning by a hydrocarbon deposit, even limited, would have been observed for the isotopic exchange.

2. *Initial Selectivity and Regioselectivity*

The above mechanism accounts for the 100% initial selectivity in D_1, whereas a multiple exchange occurs on thermally activated metal catalysts. The activated complex (Eq. 5) has an excess of energy, which dissipates during the desorption of the weakly adsorbed hydrocarbon molecule, thus allowing only one exchange act per period of adsorption.

The D_1 initial selectivity cannot result from a rapid reequilibration of polyexchanged hydrocarbon molecules as found for the thermal exchange of C_6H_6 on alumina (*5*), since no variation of D_8 was observed when it was added to the reaction mixture. This is not surprising because H atoms in alkane molecules are much less easily exchanged than those of the aromatic ring (*16*) and the reaction conditions are completely different.

The selectivity is also an indirect means of demonstrating that light energy is not merely converted into heat at the metal deposits, since otherwise a thermal and thence an initial polydeuteration activity would have been detected.

In addition to its initial selectivity in monodeuteration, photocatalytic PDIE is regioselective. From the variation kinetics of the mass peaks of the different fragments, only those which contain primary hydrogen atoms increase (Fig. 2). This means that PDIE is initially regioselective in monodeuteration of a terminal C–H bond and even the first polydeuterated propane molecules are principally labeled on the methyl groups.

For long illumination periods (Fig. 3), exchanged propane molecules can readsorb and react again in a stepwise mechanism. The first four peaks in Fig. 3 are similar to those presented in Fig. 1 of Ref. (*11*), which were obtained in the isotopic exchange of *p*-xylene with deuterium on Pt/Al_2O_3. However, although primary H atoms are preferentially exchanged, the reactivity of the secondary hydrogen atoms is not nil since perdeuteration can be reached. Kinetics calculations in a system of consecutive reactions with the same rate constant k show that (i) each intermediate goes through a maximum at a time proportional to n/k, n being the order number of the intermediate; (ii) the values of these maxima decrease regularly with n and are equidistant with a time interval proportional to k^{-1}. Figure 3 shows that the heights of the six first maxima decrease regularly and that the four first maxima are nearly equidistant. By contrast, peak D_7 culminates at a time much longer than that expected for $n = 7$. Moreover, the increase in D_7 is indicative of an accumulation due to slower kinetics.

This difference between primary and secondary H atoms has previously been found for thermal isotopic exchange over various oxide catalysts such as chromia (*1–3*), alumina (*4*), and titania (*6*). In the latter case, the exchange was accompanied by dehydrogenation. This can be accounted for by the temperature used (>700 K), since titania exhibits oxidative dehydrogenation properties at such a high temperature. In the case of chromia (1), primary H atoms were found to exchange at least six times as fast as the secondary ones. Moreover, a comparison of our results (Fig. 3) with those of Ref. (*19*) shows that a reactivity ratio of ca. 5 for the primary and secondary H atoms of propane seems reasonable. This ratio combined with the higher number of primary H atoms in C_3H_8 explains the regioselectivity in CDH_2–C_2H_5 under initial conditions when only D_1 is formed. A preferential adsorption mode of the propane molecule with one of the two methyl groups directly exposed to the surface of titania can provide a complementary explanation.

CONCLUSION

This study, in parallel with those concerning cyclopentane (*13, 14*), confirms, for the photocatalytic exchange of an alkane and deuterium over Pt/TiO_2, the real catalytic nature of the process and the initial selectivity to monodeuterated molecules. Multiple exchange is the result of the readsorption of molecules already deuterated when static reactor is used.

In addition, the regioselectivity shown here indicates that this photocatalytic method could be of value in the preparation of partially enriched deuterated alkane molecules. For instance, after 3 h under our conditions, the mixture contained 23.5% 1-deuteropropane and only 3% dideuteropropane.

REFERENCES

1. Pass, G., Littlewood, A. B., and Burwell, R. L., Jr., *J. Amer. Chem. Soc.* **82,** 6281 (1960).

2. Burwell, R. L., Jr., Haller, G. L., Taylor, K. C., and Read, J. F., *in* "Advances in Catalysis," Vol. 20, p. 1. Academic Press, New York, 1969.

3. Kalman, J., and Guczi, L., *J. Catal.* **47,** 371 (1977).

4. Robertson, P. J., Scurrel, M. S., and Kemball, C., *J. Chem. Soc. Faraday Trans. I* **71,** 903 (1975).

5. Saunders, P. C., and Hightower, J. W., *J. Phys. Chem.* **74,** 4323 (1970).

6. Halliday, M. M., Kemball, C., Leach, H. F., and Scurrel, S. M., *in* "Proceedings, 6th International Congress on Catalysis, London" (1976) (G. C.

Bond, P. B. Wells, and F. C. Tompkins, Eds.), p. 283. The Chemical Society, London, 1977.

7. Inoue, Y., Herrmann, J.-M., Schmidt, H., Burwell, R. L., Butt, J. B., and Cohen, J. B., *J. Catal.* **53,** 401 (1978).

8. Gault, F. G., Rooney, J. J., and Kemball, C., *J. Catal.* **1,** 255 (1962).

9. Burwell, R. L., Jr., *Acc. Chem. Res.* **2,** 289 (1969); *Catal Rev.* **7,** 25 (1972).

10. Barbier, J., Morales, A., and Maurel, R., *Nouv. J. Chim.* **4,** 233 (1980).

11. Hightower, J. W., and Kemball C., *J. Catal,* **4,** 363 (1965).

12. Défossé, C., Laniecki, M., and Burwell, R. L., Jr., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo" (1980), preprint B48.

13. Courbon, H., Herrmann, J. M., and Pichat, P., *J. Catal.* **72,** 129 (1981).

14. Courbon, H., Herrmann, J. M., and Pichat, P., *J. Catal.* **95,** 539 (1985).

15. Pichat, P., Mozzanega, M. N., Disdier, J., and Herrmann, J. M., *Nouv. J. Chim.* **6,** 559 (1982).

16. Shatenshtein, A. I., *in* "Isotopic Exchange and the Replacement of Hydrogen in Organic Compounds," p. 286. Consultants Bureau, New York, 1962.

17. Pichat, P., *ACS Symp. Ser.* **278,** 21 (1985); *New J. Chem.* **11,** 135 (1987).

18. Herrmann, J. M., *ACS Symp. Ser.* **298,** 200 (1986).

19. Dowie, R. S., Robertson, P. J., and Kemball, C., *J. Catal.* **35,** 189 (1974).