$(CH_2)_4 < n\text{-}C_4H_9 < CH_3 < H$. There is a general trend toward greater reactivity with increasing substitution but superposed on this are strong steric factors. Thus not only is *cis*-1,1-dichloro-2-ethyl-3-methylcyclopropane much more reactive than the *trans* isomer but 7,7-dichlorobicyclo[4.1.0]heptane, formally similar to the *cis* isomer, is even less reactive than the *trans* isomer.

The results can all be rationalized by assuming the reaction proceeds *via* a quasi-ionic transition state[21] in which the emerging cyclopropyl cation is isomerizing to an allylic cation by an electrocyclic process.[22,23] In such a mechanism the distribution of positive charge to the terminal carbon atoms of the emerging allylic system is facilitated by increasing substitution in line with the observed trend.[24] Isomerization of a cyclopropyl cation to an allylic cation is a disrotatory process so in the *gem*-dichlorocyclopropyl system the groups on the side of the ring opposite the leaving chloride ion move apart while the groups on the same side approach one another. *cis*-Dialkyl substitution permits a disrotatory process in which only hydrogen atoms move toward one another while *trans*-dialkyl substitution requires that an alkyl group approach a hydrogen atom. The substantial rate difference between *cis*- and *trans*-1,1-dichloro-2-ethyl-3-methylcyclopropane fits this picture. The low reactivity of 7,7-dichlorobicyclo[4.1.0]-heptane results because the disrotatory process where two methylene groups move toward one another is forced upon the system.[25] The alternative disrotatory process would lead to a *trans* double bond in a seven-membered ring which is even less favored.

Registry No.—Ia, 1727-64-6; IIa, 7013-11-8; IIIa, 51224-29-0; IVc, 1809-02-5; IVd, 1809-75-2; IVe, 15224-34-7; IVf, 15224-35-8.

Acknowledgment.—The infrared, ultraviolet, and nuclear magnetic resonance spectra were recorded and interpreted by Dr. F. J. Impastato.

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[21] A. Maccoll, *Advan. Phys. Org. Chem.*, **3**, 103 (1965).

[22] R. Hoffman and R. B. Woodward, *J. Am. Chem. Soc.*, **87**, 395 (1965).

[23] H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965).

[24] For experimental evidence for the validity of the predicted dispersal of positive charge and for the disrotatory nature of the transformations in solvolytic reactions of cyclopropyl halides and cyclopropyl tosylates, see S. J. Cristol, R. M. Sequeira, and C. H. DePuy, *ibid.*, **87**, 4007 (1965) and C. H. DePuy, L. G. Schnack, and J. W. Hausser, *ibid.*, **88**, 3343 (1966).

[25] P. von R. Schleyer, G. W. Van Dine, U. Schöllkopf, and J. Paust, *ibid.*, **88**, 2868 (1966).

The Rates of Hydrogenation of Cycloalkenes from the Liquid Phase on Platinum–Alumina Catalysts[1a]

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Reaction rates for the hydrogenation of 18 cycloalkenes from solution in cyclohexane on alumina-supported platinum catalysts at 25.0° near 1 atm of hydrogen are reported. These reactions are first order in hydrogen pressure and in the amount of catalyst and zero order in cycloalkene. The temperature coefficients for cyclohexene and cycloheptene are 5.7 and 6.5 kcal mole^{-1}. The data are discussed in terms of the Horiuti–Polanyi mechanism. The nonintervention of isomerization under conditions in which olefin exchange is known to be extensive, and the product to be still more extensively isotopically exchanged, leads to the proposal that platinum surfaces present two types of catalytic sites. One of these types is involved in the hydrogen addition reaction; the other with olefin exchange. The Horiuti–Polanyi mechanism for the hydrogenation of alkenes on platinum is modified to correspond.

The mechanism of the hydrogenation of alkenes at heterogeneous catalytic surfaces has been a subject of discussion for several decades.[2] Information obtained from studies using isotopic hydrogen both in exchange reactions with saturated hydrocarbons[2–4] and in the hydrogenation of alkenes[2,3,5] has particularly contributed to the present state of understanding of this reaction. Likewise, stereochemical studies have also made important contributions.[3,6] Kinetic data, on the other hand, have been limited in quantity and, particularly for hydrogenations from the liquid phase, have been of questionable applicability. Most of the pertinent kinetic data have come from studies in the gas phase using very simple alkenes.[2,3] Very little of the rate data for this reaction from the liquid phase has actually dealt with reaction kinetics and only a fraction of that which has is free from the uncertainty that the transport of hydrogen was not rate limiting.[7,8] Also, few liquid phase studies have included any particular consideration of variations in rate which result from catalyst preparation procedures,[9,10] from solvent effects, and from trace impurities. The need to control all of these variables in studies involving aromatic hy-

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[1] (a) Grateful acknowledgment is made for financial support for this research from the Petroleum Research Fund of the American Chemical Society and from the National Science Foundation. We also acknowledge the benefit derived from stimulating discussions with Professor R. L. Burwell, Jr., in the course of this research. (b) To whom inquiries should be addressed. (c) Du Pont Teaching Fellow, 1963–1964.

[2] For a recent review, see G. C. Bond and P. B. Wells, *Advan. Catalysis*, **15**, 91 (1965).

[3] G. C. Bond, "Catalysis by Metals," Academic Press Inc., New York, N. Y., 1962, Chapters 9 and 11.

[4] See (a) E. F. Meyer and C. Kemball, *J. Catalysis*, **4**, 711 (1965), and (b) K. Schrage and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **88**, 4555 (1966), for recent examples.

[5] See (a) G. V. Smith and J. R. Swoap, *J. Org. Chem.*, **31**, 3904 (1966), and (b) A. W. Weitkamp, *J. Catalysis*, **6**, 431 (1966), for recent examples.

[6] For a recent review, see S. Siegel, *Advan. Catalysis*, **16**, 123 (1966).

[7] (a) T. Freund and H. M. Hulburt, *J. Phys. Chem.*, **61**, 909 (1957); (b) R. H. Price and D. B. Schiewitz, *Ind. Eng. Chem.*, **49**, 807 (1957).

[8] (a) H. C. Yao and P. H. Emmett, *J. Am. Chem. Soc.*, **81**, 4125 (1959); (b) F. Nagy, Á. Pethö, and D. Möger, *J. Catalysis*, **5**, 348 (1966).

[9] (a) O. A. Larson, D. S. MacIver, H. H. Tobin, and R. A. Flinn, *Ind. Eng. Chem., Process Design Develop.*, **1**, 300 (1962); (b) H. Kral, *Z. Phys. Chem.*, **48**, 129 (1966).

[10] See comments of E. B. Maxted and J. S. Elkins, *J. Chem. Soc.*, 1995, 5086 (1961), concerning lack of homogeneity in catalyst preparations.

drocarbons has been pointed out[11] and one must anticipate that their effect will be greatly magnified with alkenes because the latter hydrogenate so very much faster than do aromatics.[12] In this paper we report the results of studies of the rates of hydrogenation of a number of cycloalkenes from cyclohexane solution on alumina-supported platinum catalysts of high and reproducible activity. Careful attention has been paid in these experiments to the other variables mentioned above as well; so we feel that these data can be used as a basis for a discussion of some of the details of the mechanism of this important reaction.

Results

In initial experiments using purified cyclohexene in purified acetic acid with commercial 5% platinum-alumina catalysts, the rate expression

$$\text{rate} \propto [P_{\text{H}_2}]^1[\text{catalyst}]^1[\text{cyclohexene}]^0$$

was found to apply over a wide range of reaction rate and agitation efficiency. A small, cumulative, rate-slowing effect of impurities on these catalysts was observed when several samples of cyclohexene were hydrogenated in succession and this effect was greatly exaggerated when we changed to the much more active catalysts prepared as described in the Experimental Section. This poisoning effect was time dependent and was finally traced to the acetic acid solvent; we could find no way to purify this solvent to the level required.[13]

Cyclohexane, methylcyclohexane, and octane were much more amenable to purification. The relative rates of hydrogenation of cyclohexene in these three solvents (1.00, 1.15, and 1.47, respectively) exactly parallel the solubility of hydrogen in them.[14] We finally settled on cyclohexane as the solvent of choice simply because it is available in a spectrographic grade purity and because it can be stored in the cold as a solid after being purified.

Cyclohexene Hydrogenations.—Careful attention to purification and manipulation procedures[15] (see Experimental Section) furnished data such as that presented in Figure 1. If impurities were present in such successive-sample experiments, a progressive slowing of the rates of the second and third samples was observed together with a divergence of the rate plots from linearity (Figure 2). Such data were discarded. Additional data were discarded because the rates, while constant over all three samples, were slower than we usually observed because of a reduced catalyst activity.[16] The data retained are summarized in Table I.

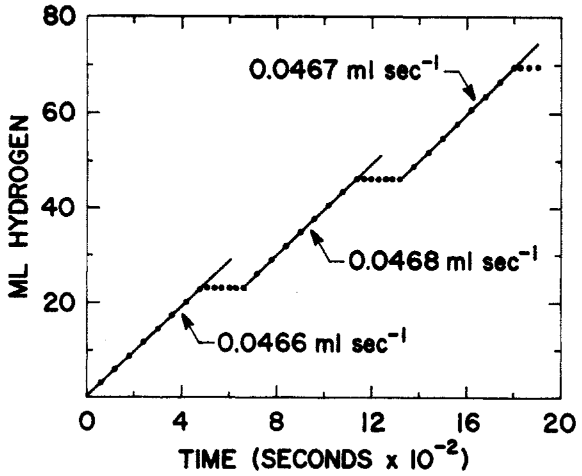

Figure 1.—Plot of hydrogen absorption: cyclohexene, 38.93 mg, 0.52% Pt, 25.0°, 770 mm.

TABLE I

HYDROGENATION OF CYCLOHEXENE IN CYCLOHEXANE AT 25°

Pressure, mm	Catalyst,[a] mg	Rate,[b] ml sec^{-1}	Specific rate[c]
751	21.15	0.0257	112
1113	21.95	0.0275	115
750	23.66	0.0267	105[d]
756	25.46	0.0310	112
747	30.41	0.0394	119
751	30.94	0.0377	113
754	32.23	0.0397	113
756	32.52	0.0416	118
770	38.93	0.0467	111
435	39.83	0.0471	110
753	40.21	0.0496	113
580	40.65	0.0505	114
751	41.76	0.0525	116
758	41.86	0.0507	112
757	42.28	0.0536	117
756	42.44	0.0531	115
742	42.50	0.0490	106
765	42.86	0.0530	114
872	44.08	0.0505	105
758	48.09	0.0577	111
757	57.56	0.0679	109
758	66.68	0.0769	106
		Av	113 ± 4[e]

[a] 0.52% Pt. [b] 25° at P_{mm}, calculated from the average of the several slopes taken from rate plots for three successive samples. [c] Moles min^{-1} g-atom^{-1} atm^{-1}. [d] Using 99% D_2. [e] Standard deviation.

Effect of Platinum Content.—The data of Table II illustrate the linear increase in catalyst *activity* with decreasing platinum content. Such trends have been noted before[9,10] and are attributable in large part to an increase in metal surface area per unit weight of catalyst.

Effect of Hydrogen Pressure.—The data of Table I show the first-order dependence of the rate of hydrogenation of cyclohexene on hydrogen pressure. These rates extrapolate to zero at zero pressure of hydrogen

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(11) See H. A. Smith in "Catalysis," Vol. V, P. H. Emmett, Ed., Reinhold Publishing Corp., New York, N. Y., 1957, p 181.

(12) (a) W. F. Madden and C. Kemball, *J. Chem. Soc.*, 302 (1961); (b) C. A. Brown and H. C. Brown, *J. Org. Chem.*, **31**, 3989 (1966); (c) R. W. Bott, C. Eaborn, E. R. A. Peeling, and D. E. Webster, *Proc. Chem. Soc.*, 337 (1962).

(13) For optimum rates, less than 10^{-3} mmole of platinum was added as the supported metal; hence, catalyst-poisoning impurities at a 10^{-3} mole % level in the 10^{-2} mole of acetic acid solvent used would exert a marked slowing effect with these active catalysts.

(14) P. Frolich, E. J. Tauch, J. J. Hogan, and A. A. Peer, *Ind. Eng. Chem.*, **23**, 548 (1931). See also M. W. Cook, D. N. Hanson, and B. J. Alder, *J. Chem. Phys.*, **26**, 748 (1957).

(15) When the same syringe was used to inject a second and a third sample of cyclohexene, hydrogen-uptake rates slowed and diverged from linearity in a cumulative way. This is presumably the result of peroxide formation in amounts detectable only by their poisoning effect on these very active hydrogenation catalysts.

(16) This decrease in catalyst activity was the result of the accumulation of water by adsorption on the support. The original activity could be restored by heating the catalysts in hydrogen at 300° for a few hours; exposure to humid atmospheres lead to an increase in weight and a proportional decrease in *specific* activity.

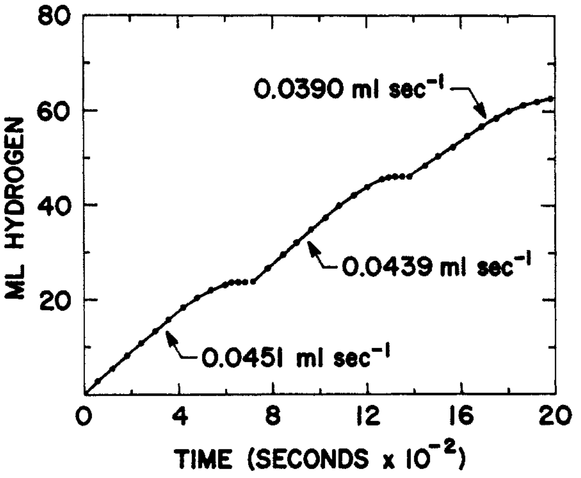

Figure 2.—Plot of hydrogen absorption: cyclohexene, 40.06 mg, 0.52% Pt, 25.0°, 758 mm, trace impurities present.

TABLE II

EFFECT OF PLATINUM CONTENT OF CATALYSTS ON CYCLOHEXENE HYDROGENATION

% Pt	Specific rate[a]
1.11	76 ± 1 (3)
0.97	81 ± 2 (13)
0.72	96 ± 1 (3)
0.64	104 ± 4 (11)
0.52	113 ± 4 (30)
0.49	117 ± 2 (3)
0.39	121 ± 1 (2)

[a] As in Table I. Number of experiments in parentheses. P_{H_2} = 760 ± 10 mm.

and a least-squares log rate *vs.* log P_{H_2} plot, a very sensitive test for kinetic order, has a slope of 1.0. Cycloheptene responded to changes in hydrogen pressure in the same way. We have less extensive measurements for the other cycloalkenes of Table III but these data show them to exhibit a similar first-order dependence on hydrogen pressure. The reliability is high, however, because these data were obtained from experiments in which two samples of cyclohexene bracketed a sample of the other alkene.

Other Cycloalkenes.—The rates of hydrogenation of 17 additional cycloalkenes at 25.0° near 1 atm of hydrogen are summarized in Table III. These rates were determined in experiments in which the cycloalkene sample was both preceded and followed by a sample of cyclohexene. This procedure furnished an automatic check for catalyst activity.[16] It also revealed the presence of inadvertent impurities in the system by a slowing of the second cyclohexene sample and a curvature in its rate plot. The data were discarded if the rates of both cyclohexene samples were not exactly the same, if their rate plots were not linear, or if they were less than 90% of the average of Table I. If both cyclohexene samples bracketing a sample of another alkene gave rates which were only slightly low but were otherwise acceptable, the rate for the interposed alkene was corrected by the cyclohexene rate factor. A few of such corrected data are included in Table III.

The specific rates in Table III are expressed in terms of our 0.52% Pt catalyst. However, rate measurements for several of the cycloalkenes which hydrogenate more slowly than 1-methylcyclopentene were also carried out using a 0.97% catalyst as well as the 0.52% one. The two specific rates are interconvertible by the factor 113/81 (specific rates for cyclohexene; see Table II) and some of these data are included in Table III.

TABLE III

HYDROGENATION OF CYCLOALKENES IN CYCLOHEXANE AT 25° AND 1 ATM

Cycloalkene[a]	Registry no.	Specific rate[b]
Bicyclo[2.2.1]C_7 (3)	498-66-8	223 ± 10
Bicyclo[2.2.2]C_8 (4)	931-64-6	174 ± 5
3-Methyl C_5 (2)	1120-62-3	153 ± 9[c]
Methylene C_6 (2)	1192-37-6	131 ± 6[c]
C_5 (5)	142-29-0	121 ± 2
C_6 (30)	110-83-8	113 ± 4
3-Methyl C_6 (4)	591-48-0	103 ± 2[c]
4,4-Dimethyl C_6 (3)	14072-86-7	100 ± 1[c]
4-Methyl C_6 (4)	591-47-9	94 ± 4[c]
1-Ethyl C_5 (6)	2146-38-5	88 ± 4
1-Methyl C_5 (4)	693-89-0	85 ± 1
C_7 (5)	628-92-2	78 ± 3
Ethylidene C_5 (2)	2146-37-4	59 ± 1[d]
1-Methyl C_6 (4)	591-49-1	57 ± 6
Ethylidene C_6 (4)	1003-64-1	40 ± 1[c]
1-Methyl C_7 (3)	1453-25-4	34 ± 1
1-Ethyl C_6 (3)	1453-24-3	19 ± 1
C_8 (4)	931-88-4	10 ± 1

[a] Number of determinations in parentheses. [b] As in Table I; 0.52% Pt catalyst; standard deviations where five or more separate determinations; deviation from the mean for others. [c] No detectable isomerization during hydrogenation. [d] Significant isomerization to 1-ethylcyclopentene; specific rates calculated from initial rates; $\text{rate}_{H_2\text{ addn}}/\text{rate}_{\text{isomerizn}} \cong 5$.

Several of the cycloalkenes (3-methylcyclopentene, methylenecyclopentane, 3-methylcyclohexene, 4,4-dimethylcyclohexene, 4-methylcyclohexene, ethylidinecyclopentane, and ethylidenecyclohexane) are thermodynamically unstable relative to an isomeric counterpart.[17] Samples removed in the course of their hydrogenation revealed the intervention of isomerization only with ethylidenecyclopentane when 1-ethylcyclopentene was observed to be present throughout the hydrogenation. The hydrogenation–isomerization ratio, determined by analysis of the mixture during the early stages of the reaction, was approximately 5. Isomerization of the other cycloalkenes, if any, was less than the 0.1% we could detect by our glpc analytical procedures.

The specific rate recorded for 1-methylcyclohexene is subject to some uncertainty. We could not purify this cycloalkene to the point where the hydrogenation of the second sample of cyclohexene was as fast as the first. The value given is the average of the four fastest rates observed in 10 measurements using this alkene. None of the other cycloalkenes was as intractable.

Temperature Coefficient.—Detailed studies of the effect of temperature in this reaction were carried out only with cyclohexene and cycloheptene. The results are summarized in Table IV and Figure 3. These specific rates have been corrected for the change in partial pressure of hydrogen, as a result of the change in vapor pressure of cyclohexane,[18] and for the change of solubility of hydrogen with temperature.[14] The apparent activation energies for the hydrogenation of cyclohexene and cycloheptene, calculated from the

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(17) E. Gil-Av and J. Shabtai, *Chem. Ind.* (London), 1630 (1959).

(18) "International Critical Tables," Vol. III, p 222.

TABLE IV

EFFECT OF TEMPERATURE ON THE HYDROGENATION OF CYCLOHEXENE AND CYCLOHEPTENE

T, °K	Specific rate[a,b] (C_6)	Specific rate[a,b] (C_7)
291.1	63	38
298.1	81	53
299.2	82	52
307.5	102	73
307.9	108	76
316.1	135	96
317.6	151	103

[a] As in Table I but using our 0.97% Pt catalyst. [b] Corrected for the change in vapor pressure of cyclohexane and the solubility of hydrogen with temperature.

slopes of the plots in Figure 3, are 5.7 and 6.5 kcal mole^{-1}, respectively.

Discussion

Three separate steps are involved in the hydrogenation of an alkene in the liquid phase on a heterogeneous catalyst: step 1, the transport of gaseous hydrogen into the liquid phase and the diffusion of hydrogen and the alkene through the solution to the catalytic surface; step 2, the chemisorption of these reactants, their reaction at the surface, and their associative desorption as product; and step 3, the diffusion of the product away from the catalyst. It is the details of step 2 which are of greatest mechanistic significance; hence, it is necessary to know that neither step 1 nor step 3 is rate limiting. It has been shown[19] that the rate of diffusion of alkenes through the solution to the catalyst and of product away from it exceeds the rate at which hydrogen reaches the catalytic surface. From diffusion coefficients for hydrogen and cycloalkenes in cyclohexane[20] and their concentrations,[14] it can be predicted that this condition will continue to exist until hydrogenation is almost complete. Therefore hydrogen diffusion will be responsible if diffusion through the solution actually controls the reaction kinetics. Control by hydrogen transport from the gas phase into the liquid phase at rates below 5 ml min^{-1} is ruled out by the data of Table I: if agitation were not sufficient to maintain a constant concentration of hydrogen in the liquid phase which approaches the equilibrium value,[7,8a] the observed rates would not be first order in the amount of catalyst present in the system. This limit is not reached with our agitator and creased flask system below 10 ml min^{-1} for cyclohexene, but at hydrogen demand rates above 16 ml min^{-1}, the observed rates become *independent of the amount of catalyst* (*i.e.*, transport of hydrogen into the liquid phase then becomes rate controlling).

Likewise, the data of Table III encompass a wide range of hydrogen demand rates at the catalyst surface between that for the very slow cyclooctene to that of bicycloheptene. Diffusion of hydrogen through the solution to the catalyst surface therefore cannot be rate controlling for any of the cycloalkenes which hydrogenate more slowly than bicyclo[2.2.1]heptene so long as fewer than 10 ml min^{-1} of hydrogen are required to be transported across the gas–liquid interface in our system. The reaction kinetics reported

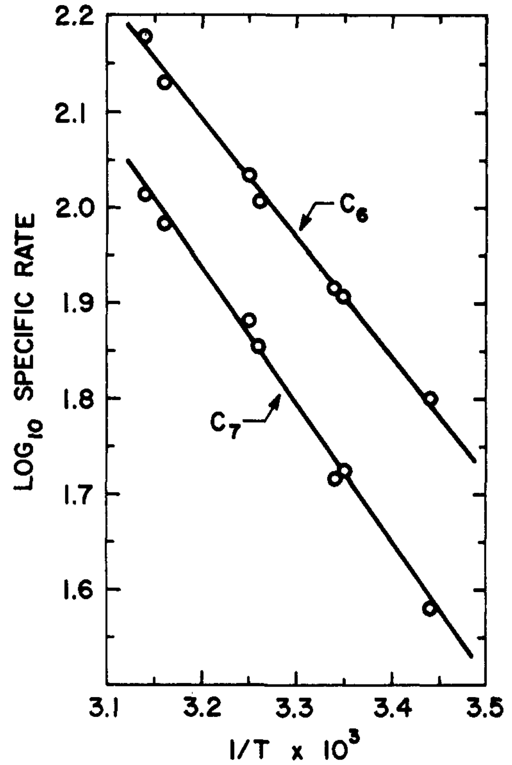


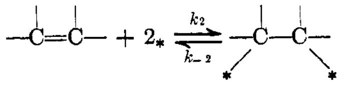
Figure 3.—Plot of log specific rate *vs.* $1/T \times 10^3$ from Table IV.

here, therefore, pertain to the processes of step 2. We propose to consider the significance of these kinetic data, using the Horiuti–Polanyi mechanism[21] (1–4) as a framework for our discussion. We will regard the last step in this mechanism as irreversible as long as any alkene remains.

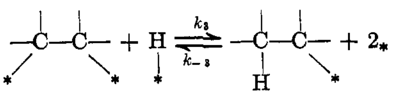
$$H_2 + 2_* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2H_*$$

dissociative adsorption[22] (1)

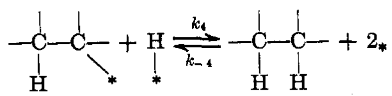
Cycloalkene Molecularity.—The observed zero-order dependence of the rate expression on cycloalkene concentration can be interpreted in terms of the Langmuir adsorption isotherm to mean that these alkenes are strongly adsorbed on platinum surfaces. In terms of the Horiuti–Polanyi mechanism, such zero-order kinetics requires that $k_2 \gg k_{-2}$ so that the catalyst, in effect, remains saturated with chemisorbed alkene throughout the hydrogenation. In this research, however, we were unable to detect any double-bond migration during the hydrogenation of the several



dissociative adsorption (2)



associative reaction (3)



associative desorption (4)

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(19) G. C. Bond and J. S. Rank, *Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, 1964*, 1225 (1965).

(20) J. H. Arnold, *J. Am. Chem. Soc.*, **52**, 3937 (1930).

(21) M. Polanyi and J. Horiuti, *Trans. Faraday Soc.*, **30**, 1164 (1934).

(22) We use the terminology proposed by R. L. Burwell, Jr., *Chem. Eng. News*, **44**, 56 (1966). The corresponding terminology for the reverse processes are *associative desorption* for eq 1 and 2 and *dissociative reaction* and *dissociative adsorption*, respectively, for eq 3 and 4.

cycloalkenes of Table III which can isomerize to more stable and more slowly hydrogenated isomers. In the single instance where isomerization was observed (ethylidenecyclopentane), the isomer formed (1-ethylcyclopentene) is a more stable one, but it is also the more rapidly hydrogenated. As a consequence of our failure to observe any intervention of isomerization (with the single, extraordinary exception), we are forced to inquire whether one or the other of Horiuti–Polanyi reactions 2 and 3 with most alkenes should not be represented as irreversible.

On the one hand, the extensive olefin exchange and the additional exchange in the saturated product which are observed when deuterium is used under hydrogenation conditions very similar to ours[5,23] offer strong support for describing both reactions 2 and 3 as reversible processes on platinum surfaces. The extent of this exchange implies that more than one-fifth, perhaps as much as one-half, of the chemisorbed alkene returns to the solution after it has taken part in surface reactions in which C–H bonds have been made and broken.[5,23] Accordingly, Horiuti–Polanyi reactions 2 and 3 must be viewed not only as reversible but, with some alkenes, to approach an equilibrium condition. On the other hand, isomerization of alkenes during their hydrogenation on platinum catalysts has also been found by others to be very minor[23,24] and racemization of (+)-1-*p*-menthene not to occur.[5a] Thus there appears to be equally strong support for the contention that Horiuti–Polanyi reactions 2 and 3 cannot both be reversible processes on platinum surfaces.

To solve this dilemma we propose that platinum surfaces, in common with palladium,[25] present more than one type of site for the chemisorption and the surface reactions of alkenes. Specifically, we propose (a) that one type of platinum site effects the olefin exchange reaction and returns exchanged but unisomerized alkene to the solution;[23,26] (b) that another type catalyzes the hydrogen addition reaction *via* a Horiuti–Polanyi mechanism modified to have reaction 2 as irreversible; and (c) that these are two entirely independent sets of surface reactions on platinum. We will first consider the implications of this proposal relative to the olefin exchange reaction.

Of the possible pathways which can lead to olefin exchange, only those which involve a dissociatively 1-monoadsorbed (*i.e.*, vinyl) or 3-monoadsorbed (*i.e.*, allyl) surface species[23] are consistent with the nonintervention of isomerization[23,24] and racemization.[5a] A π-allyl surface species[27] is not a suitable intermediate, nor is a concerted process, which abstracts an allylic hydrogen while simultaneously adding another to the remote olefinic carbon,[28] a suitable pathway. Likewise, a 1,3 topside hydrogen shift[5a] would require racemization of (+)-1-*p*-menthene and isomerization of other alkenes. Most important, coupled, reversible Horiuti–Polanyi reactions 2 and 3 cannot be involved in the olefin exchange reactions. The olefin exchange reactions and the hydrogen addition reactions implicit in the Horiuti–Polanyi mechanism are therefore more rationally viewed as entirely separate processes and it is then reasonable to conclude that the two sets of surface reactions take place on different sets of sites.

Turning our attention to the hydrogen addition reactions, the additional exchange observed in the saturated product[5,23,26] seems clearly to require that reaction 3 be reversible or that some equivalent process (a π-allyl surface species[27] or a concerted process[5a,28]) take place. In any event, reaction 2 must then be an effectively irreversible step in the hydrogen addition reactions on platinum surfaces. We propose that the very weakly chemisorbed and slowly hydrogenated tetrasubstituted alkenes (*e.g.*, 1,2-dimethylcyclohexene[29] and $\Delta^{9,10}$-octahydronaphthalene[5b,23,30]) may be exceptional and that certain unstable alkenes for which facile pathways to isomerization exist (*e.g.*, ethylidenecyclopentane in this research and *trans*-cyclodecene[31]) may be others, but such alkenes are exceptions and the chemisorption of most alkenes on the platinum surface sites which promote hydrogen addition is effectively irreversible. In contrast, chemisorption of alkene on olefin exchange sites is highly reversible.

Hydrogen Molecularity.—When heterogeneous catalysts with an extensive internal pore structure are used, diffusion of the reactants within the pores (a first-order process) may control the kinetics of the reaction and the experimentally observed kinetic parameters may then be spurious.[32] However the *intrinsic* order, n, of a reactant in such circumstances is related to the observed order, m, by $n = 2m - 1$; so we are observing an *intrinsic* first-order hydrogen dependence regardless of how small a fraction of the total catalytic surface is actually utilized.[33] We can then interpret the first-order dependence of rate on hydrogen pressure in terms of the Langmuir adsorption isotherm to mean that hydrogen is very weakly chemisorbed on platinum relative to the cycloalkenes; hence, the fraction of the surface occupied by hydrogen is relatively small. The first-order dependence also implies that two hydrogen atoms are involved in the rate-critical transition state. Two extremes are in accord with such circumstances: (a) a very fast hydrogen addition reaction such that hydrogen chemisorption is rate limiting and (b) a very slow hydrogen addition reaction so that hydrogen chemisorption is effectively at equilibrium. At the first extreme the rate expression in terms of Horiuti–Polanyi reactions 1–4 is

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(23) G. V. Smith and R. L. Burwell, Jr., *J. Am. Chem. Soc.*, **84**, 925 (1962).

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(33) The small apparent activation energies of 5.7 and 6.5 kcal mole^{-1} that we observe for cyclohexene and cycloheptene suggest that the reaction kinetics may well be controlled by pore diffusion of hydrogen, however.

$$\text{rate} = k_1P_{\mathrm{H_2}} \quad \text{(i)}$$

and at the second

$$\text{rate} = k_4K_1P_{\mathrm{H_2}} \quad \text{(ii)}$$

It is unlikely that the hydrogenation of any of the cycloalkenes in this study involves conditions close to either of these extremes, however. Rather, it seems more likely that the slowest of these through the fastest encounters conditions which cover a range somewhere in between. It is then not immediately obvious why a first-order hydrogen dependence should be observed.

It is consistent with the observed kinetics to consider a platinum hydrogenation surface to be very largely occupied by hydrocarbon as diadsorbed (E) and monoadsorbed alkane (HE), leaving a small and constant increment which is accessible only to hydrogen. Since chemisorption of alkene is very fast, we can define the surface occupied by hydrocarbon species in terms of fractions, θ, by

$$\theta_{\mathrm{E}} + \theta_{\mathrm{HE}} = 1 \quad \text{(iii)}$$

The residual surface inaccessible to hydrocarbon which is occupied by hydrogen atoms (H) and vacant (MTH) can be similarly defined by

$$\theta_{\mathrm{H}} + \theta_{\mathrm{MTH}} = 1 \quad \text{(iv)}$$

Applying the steady-state approximation[34] to θ_{HE} using rate constants corresponding to Horiuti–Polanyi reactions 1–4, one obtains

$$d\theta_{\mathrm{HE}}/dt = k_3\theta_{\mathrm{H}}\theta_{\mathrm{E}} - k_{-3}\theta_{\mathrm{HE}} - k_4\theta_{\mathrm{H}}\theta_{\mathrm{HE}} \cong 0 \quad \text{(v)}$$

In combination with the rate expression

$$\text{rate} = d[\mathrm{H_2E}]/dt = k_4\theta_{\mathrm{H}}\theta_{\mathrm{HE}} \quad \text{(vi)}$$

iii and v give

$$\text{rate} = k_3k_4\theta_{\mathrm{H}}^2/[k_{-3} + (k_3 + k_4)\theta_{\mathrm{H}}] \quad \text{(vii)}$$

A rigorous solution of vii requires the solution of the cubic equation obtained from eq v and the steady-state expression for θ_{H}

$$d\theta_{\mathrm{H}}/dt = k_1P_{\mathrm{H_2}}\theta_{\mathrm{MTH}}^2 - k_{-1}\theta_{\mathrm{H}}^2 - k_3\theta_{\mathrm{H}}\theta_{\mathrm{E}} + k_{-3}\theta_{\mathrm{HE}} - k_4\theta_{\mathrm{H}}\theta_{\mathrm{HE}} \cong 0 \quad \text{(viii)}$$

We avoid this imposing task by making the reasonable simplifying assumption that θ_{H} is proportional to $(k_1P)^{1/2}$ at pressures near 1 atm. The rates of hydrogenation are then seen from eq vii to be first order in hydrogen but to differ as a result of variations in the rate constants k_3, k_{-3}, and k_4 for one alkene as compared to another. When $k_{-3} \ll (k_3 + k_4)\theta_{\mathrm{H}}$, a square-root dependency on hydrogen pressure would be observed and in that sense Horiuti–Polanyi reaction 3 might be described as the rate-limiting step[35] when this condition exists. Otherwise there is no single step in the hydrogenation of alkenes on platinum surfaces which can be pointed to as rate limiting except in the extreme conditions where eq i or ii applies.

Experimental Section

Hydrogenation Apparatus.—Hydrogenations were carried out in a system which could be adjusted to operate at constant pressure (±1 mm) between 200 and 1200 mm. The changing level of butyl phthalate in a differential manometer interposed between a thermostat-jacketed hydrogenation system and a thermostat-jacketed gas ballast of equal volume actuated a capacitance relay, thence a solenoid gas valve, to allow nitrogen from a 10-l. surge tank at 1-atm superpressure to drive the mercury-retaining fluid into a jacketed gas buret. A long-stem needle valve in the line made it possible to smooth the flow of nitrogen from the surge tank, hence of the mercury into the gas buret, with a resulting improvement in the accuracy of volume readings. Temperatures were maintained at preset values within ±0.1° by circulation of water from a constant-temperature bath. This system is a variation of one previously described.[7a]

The jacketed reaction flasks (10- and 25-ml bulb volumes) had cone-shaped bulbs with an impressed crease and a side-arm entry through a silicone septum for the introduction of reactants or removal of sample. The flasks were agitated by an eccentric (3 mm off-center) keyed to the shaft of a 1750-rpm motor. The attitude of creased flasks to the eccentric seat was not critical but vortices developed when flasks without the crease were positioned in certain ways. Experiments showed that the visual agitation efficiency with the creased flasks could be varied widely at hydrogen demand rates up to 7 ml min^{-1} and above without effecting a change in rate. Most of the data collected involved 1–5-ml min^{-1} hydrogen consumption.

Electrolytic hydrogen was used throughout after being purified by passage through a deoxygenating unit, thence through columns of silica gel and a Linde 3A Molecular Seive.

Catalysts.—Alumina for use as the catalyst support was prepared from high-purity aluminum wire and calcined under oxygen in a tube furnace at 600° ± 10° for 4 hr to give η-alumina. This was then pulverized and sieved and that retained between 150 and 200 mesh sieves was used as the catalyst support. The alumina prepared in this way had a surface of 187–190 m^2/g as determined by the procedure of Loebenstein and Dietz.[36]

Dinitrodiamineplatinum (II)[37] from high-purity platinum wire was recrystallized from four to six times from water. A hot, nearly saturated aqueous solution of the platinum complex was stirred with the alumina in a short, separable chromatography column. After standing for 15 min at 90–95°, the column was drained and the hot eluate was percolated through the alumina column three times. The eluate was then used five more times in a repetition of these operations, after which the column was rinsed with three portions of water. The alumina plug was then expressed into a Vycor boat and dried by heating in an oven at 130° for 2 hr. The dried alumina plug was heated in a tube furnace in a stream of oxygen at 500 ± 10° for 4 hr, after which the system was cooled under high-purity nitrogen to 350 ± 10°. The catalyst was then activated by heating at 350 ± 10° for 18 hr under a stream of oxygen-free electrolytic hydrogen. The platinum content of the catalyst was determined by a spectrophotometric procedure[38] using differential spectrophotometry[39] to improve the precision.[40]

The fraction of the platinum complex deposited on the alumina varied from one-tenth to one-third in several preparations. As a consequence, exact duplication of the platinum content of these catalysts was purely by chance. When a solution of the complex was merely stirred with the alumina and the whole evaporated, some bulk platinum always adhered to the side of the Vycor boat and the catalyst was not homogeneous in platinum content or in activity.[10]

Solvents.—Spectroscopic grade cyclohexane was distilled through a 100-plate fractionating column. The main fraction was further purified by passage through 18 ft of silicone 200 on 60–80 mesh firebrick in a preparative gas chromatograph to give material of complete single peak purity when analyzed by passage through an analytical gas chromatograph. This material was then distilled from potassium metal and stored under nitrogen in tightly sealed containers at −5°. Immediately before use, the 1 ml of completely pure solvent needed for an experiment was

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[34] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p 104.

[35] See ref 6, p 138.

[36] W. V. Loebenstein and V. R. Dietz, *J. Res. Natl. Bureau Std.*, **46**, 2174 (1951).

[37] M. Vezes, *Bull. Soc. Chim. France*, **21**, 481 (1899); L. A. Chugaev and S. S. Kiltonovich, *J. Chem. Soc.*, **109**, 1286 (1916).

[38] I. Mazekien, L. Ermanis, and T. J. Walsh, *Anal. Chem.*, **32**, 645 (1960).

[39] C. F. Hiskey, *ibid.*, **21**, 1440 (1949); C. N. Reilley and C. M. Crawford, *ibid.*, **27**, 716 (1955).

[40] We are indebted to Dr. Donald A. Keyworth, Universal Oil Products Co., Des Plaines, Ill., for the determination of the platinum content of several of these catalysts by atomic absorption analysis, a procedure of considerably greater precision.

obtained by percolating 2 ml of this purified material through a 10 × 20 mm column of activated alumina under nitrogen.

Methylcyclohexane and octane were purified in the same way. We could not purify acetic acid to the degree of purity required for these rate measurements.

Cycloalkenes.—The best commercially available cycloalkenes were purified in the same way as the hydrocarbon solvents and tightly sealed in containers under nitrogen. Immediately before use, the 0.1–0.3 ml of completely pure cycloalkene needed for an experiment was obtained by percolating 0.5 ml of carefully purified cycloalkene through a 10 × 10 mm column of alumina under nitrogen.

Samples of purified alkene which had been stored under nitrogen at −5° for more than 2 days were repurified as above before being used. Samples stored for 3 or 4 days always contained catalyst-poisoning impurities which slowed the hydrogen uptake rates and caused a divergence of the rate plots from linearity, as in Figure 2.

Hydrogenations.—In a typical experiment, 38.93 ± 0.05 mg of 0.52% platinum–alumina catalyst was added to the reaction flask. The flask was then attached to the apparatus and evacuated at 0.1 mm for 20 min while the system came to temperature equilibrium at 25.0 ± 0.1°. The system was then flushed five times with hydrogen. The addition of 0.60 ± 0.01 ml of freshly purified cyclohexane through the septum was followed by 5–10-min agitation in hydrogen at atmospheric pressure. A 0.100 ± 0.002 or 0.200 ± 0.002 ml sample of freshly purified cyclohexene was then injected, the pressure control system was quickly adjusted to 760 ± 10 mm, and agitation was started. The volume of hydrogen in the gas buret was read to the nearest 0.1 ml at 30-sec intervals. When the hydrogenation of the first sample was complete, a second sample was added using a clean hypodermic syringe and its hydrogenation was followed as above. A third sample of cyclohexene was then injected. If the rates were not constant over all three samples or if the rate plots diverged from linearity (see Figures 1 and 2), the data were discarded. An average of several values for the slopes of the linear rate plots was used to calculate the specific rates.

The rates of hydrogenation of the other cycloalkenes (Table III) were determined by substituting a sample for the middle cyclohexene sample in the experiment described above.

Temperature and Pressure Studies.—A number of hydrogen pressure dependency studies were performed using cyclohexene and cycloheptene in similar successive-sample rate measurements, but only a limited number of hydrogen dependency experiments were performed with the other cycloalkenes. Careful studies of temperature dependency were also limited to cyclohexene and cycloheptene. These studies involved three successive samples of the cycloalkene and the requirement that the observed rates be constant over all three samples.

Oxidation of Olefins by Supported Chromium Oxide

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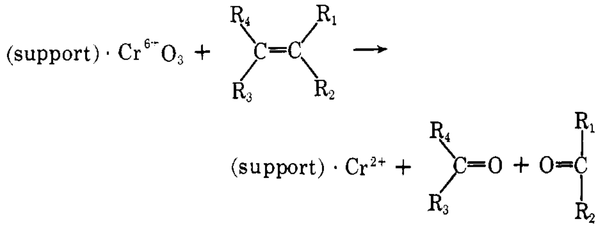
Olefins react with chromium trioxide supported on silica or silica–alumina to give oxidative cleavage of the double bond, with formation of the corresponding aldehydes and ketones as primary oxidation products. The chromium is reduced to the divalent state, apparently in a one-step process. A concerted mechanism is proposed to explain the observed specificity.

In the course of a general study of a variety of catalytic processes, the reaction between olefins and chromium trioxide supported on silica or silica–alumina was examined.[2] Somewhat surprisingly it was found that the supported chromium trioxide reacts rapidly and specifically with olefins to cause cleavage of the double bond and formation of the corresponding carbonyl compounds according to eq 1.



(1)

It is well known that chromium trioxide is a powerful oxidizing agent which reacts with many organic compounds, usually giving a variety of products.[3] Therefore, the observed specificity of the supported system was sufficiently unique to warrant additional investigation of the reaction mechanism.

Experimental Section

Materials.—The silica and silica–alumina used in this work were finely divided sands of ~600 m^2/g surface area, supplied by Davison Chemical Co. The supports were impregnated with an aqueous solution of chromium trioxide of appropriate concentration such that, after removal of excess impregnating solution and drying, the desired chromium level was obtained. In this work, composites containing 0.5 and 2.5% chromium were used.

Dehydration of Supported Chromium Trioxide.—The dehydration system consisted of a 2-ft section of 1-in.-diameter Vycor tubing equipped with a gas inlet, a thermocouple well, a trap at the top to collect fines, and provision to remove the product without exposure to the air. The unit was vertically mounted in an electric furnace which was equipped with a time switch to turn off the heat at the end of a preselected cycle. In most cases the composite was treated by fluidization in a stream of dry air or oxygen for 6 hr. After treatment the sand was orange or yellow.

Reaction of Ethylene with Oxides of Chromium.—The standard procedure involved heating a weighed sample of the chromium compound in an ethylene atmosphere within a glass tube of known volume equipped with a stopcock to allow sampling of the vapor space. Ethylene (40 cc at 380 mm) was heated at 200° for 16 hr over 1.0 g of finely ground chromium trioxide (Baker Analytical Grade Reagent). Periodic sampling of the vapor space and analysis by gas–liquid partition chromatography revealed an amount of carbon dioxide proportional to the period of heating, *e.g.*, after 2 hr, 36% of the olefin had been oxidized. At 250°, the oxidation of ethylene was complete within 1 hr. No evidence of ethylene polymerization was found.

In another experiment, ethylene was contacted at 150° with chromium trioxide which had been previously heated in a stream of dry air at 450° for 10 hr to afford decomposition[4] to a mixture of Cr^{3+} and Cr^{6+}. Gas chromatographic analysis revealed only ethylene present in the vapor space. At 250°, a small amount of carbon dioxide was formed indicating the presence of low concentrations of Cr^{6+}. At neither temperature was there any indication of polymerization.

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(1) Address inquiries to this author.

(2) A preliminary report of this work is covered in U. S. Patent 3,201,476 (1965), issued to the same authors.

(3) A. Byers and W. J. Hickinbottom, *J. Chem. Soc.*, 1334 (1948).

(4) M. J. Udy, "Chromium," Vol. I, Reinhold Publishing Corp., New York, N. Y., 1956.