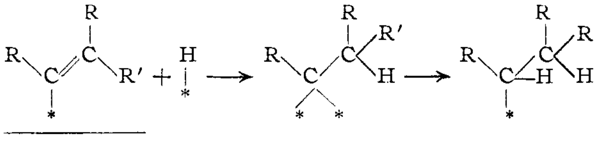
occur *via* transition states whose probable geometry conforms to the above principle.

The surface reactions in which carbon to hydrogen bonds are formed appear to be analogous to the electrophilic displacement reactions on carbon atoms which take place with retention of configuration.[22-24] In this transition state, the molecular orbital joining the carbon atom to the surface is divided so as to overlap both a surface orbital and the hydrogen atom being removed from the surface.

Of the possible one-step transformation products of the "stereochemically symmetrical intermediate" which would not yield an alkene directly but would be a reasonable step along the path toward saturation, the following appears to us to be most likely[25]



Because the π-orbital in H is directed parallel to the surface, it is not properly oriented to rehybridize in a manner which will both overlap with a hydrogen atom leaving the surface and the second indicated surface orbital without a *prior* destruction of the π-bond.

This reaction path would, therefore, be expected to have a higher energy barrier than one yielding the alkene directly.

In conclusion, the data and arguments presented here are consistent with the Horiuti–Polanyi mechanism for the hydrogenation of unsaturated hydrocarbons on an active surface.[26] Our study shows how the stereochemistry of the reaction may be employed to define the rate-limiting surface reaction as well as to describe the geometry of the pertinent transition states.

---

(22) S. Winstein and T. Traylor, *J. Am. Chem. Soc.*, **78**, 2597 (1956).

(23) H. B. Charman, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 2530 (1959).

(24) M. M. Kreevoy and R. L. Hansen, *J. Am. Chem. Soc.*, **83**, 626 (1961).

(25) R. L. Burwell, Jr., *Chem. Revs.*, **57**, 895 (1957).

(26) For a detailed review of the literature, see T. I. Taylor, "Catalysis," Vol. V, edited by P. H. Emmett, Reinhold Publishing Corp., New York, N. Y., 1957, Chap. 5.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ARKANSAS, FAYETTEVILLE, ARK.]

The Stereochemistry of the Hydrogenation of the Isomeric Xylenes and *p-tert*-Butyltoluene over a Platinum Catalyst[1,2,3]

BY S. SIEGEL, G. V. SMITH, B. DMUCHOVSKY, D. DUBBELL AND W. HALPERN

RECEIVED OCTOBER 25, 1961

The ratio of *cis* and *trans* disubstituted cyclohexanes which is obtained from the hydrogenation of the isomeric xylenes and *p-tert*-butyltoluene, dissolved in acetic acid and in contact with reduced platinum oxide, is a function of the structure of the substrate and the pressure of hydrogen. The proportion of the *cis* isomer increases with an increase in the pressure of hydrogen for pressures over two atmospheres. At lower pressures the ratio changes in a manner characteristic of the individual aromatic hydrocarbon. A comparison of these data with the stereochemistry of the hydrogenation of the related cycloalkenes suggests that the latter are intermediates in the reduction of the aromatic cycle.

Introduction

The stereochemistry of the hydrogenation of an aromatic compound, diphenic acid, was the subject of a series of papers presented almost twenty years ago by Linstead and his students.[4] Their results suggested that when an aromatic cycle was reduced during a single period of adsorption on the catalyst, it gave rise to stereoisomers in a proportion determined by steric interaction between the substituents on the cycle and the catalyst. They recognized that some aromatic compounds produced intermediate reduction products which were released from the surface, *e.g.*, cyclohexanone from the reduction of phenol.[5,6] We have sought to provide detailed stereochemical information with simple disubstituted benzenes and related cyclohexenes to examine the extent to which the stereochemistry of the latter, which are possible intermediates, might account for the results.[7,8] Work which we reported earlier was subject to more limited analytical techniques than are now available but indicated the major stereochemical trends.[7]

Experimental

Materials.—The *o*- and *m*-xylenes were the Research-Grade obtained from the Phillips Petroleum Co. and were stated to be at least 99.8% pure. *p*-Xylene was purified by repeated crystallization, the material used having the properties, m.p. 12.3–12.6°, $n^{25}\text{D}$ 1.4936, lit.[9] m.p. 13.2°, $n^{25}\text{D}$ 1.4932. *p-tert*-Butyltoluene was carefully fractionated on a column rated at 90 theoretical plates. A center cut, b.p. 191–192°, which was free of impurities by g.l.c. analysis, was used.

Apparatus and Procedures.—Three types of hydrogenation apparatus were used, depending on the pressure of the hydrogen; at high pressures (40–300 atm.), a rocker-type high pressure bomb (American Instrument Co., Inc.); for intermediate pressures (2–4 atm.), a Parr low pressure hydrogenation apparatus (Parr Instrument Co., model A, no. 112); and at low pressures (0.25–1 atm.), a semi-micro constant pressure hydrogenation apparatus.[10]

---

(1) The support by a grant from the National Science Foundation is gratefully acknowledged.

(2) Presented before the Petroleum Division at the 140th Meeting of the American Chemical Society, Chicago, Ill., September, 1961.

(3) S. Siegel and B. Dmuchovsky, *J. Am. Chem. Soc.*, **84**, 3132 (1962).

(4) R. P. Linstead, W. von E. Doering, S. B. Davis, P. Levine and R. R. Whetstone, *ibid.*, **64**, 1985 (1942), *et sequitur*.

(5) G. Vavon, *Bull. soc. chim.*, [4] **41**, 1253 (1927).

(6) J. C. Jungers and F. Coussemant, *J. chim. phys.*, **47**, 139 (1950).

(7) S. Siegel and M. Dunkel, "Advances in Catalysis," Vol. IX, Academic Press, Inc., New York, N. Y., 1956, p. 15.

(8) S. Siegel and G. S. McCaleb, *J. Am. Chem. Soc.*, **81**, 3655 (1959).

(9) J. D. White and F. W. Rose, Jr., *J. Research Natl. Bur. Standards*, **9**, 717 (1932).

(10) S. Siegel and G. V. Smith, *J. Am. Chem. Soc.*, **82**, 6082 (1960).

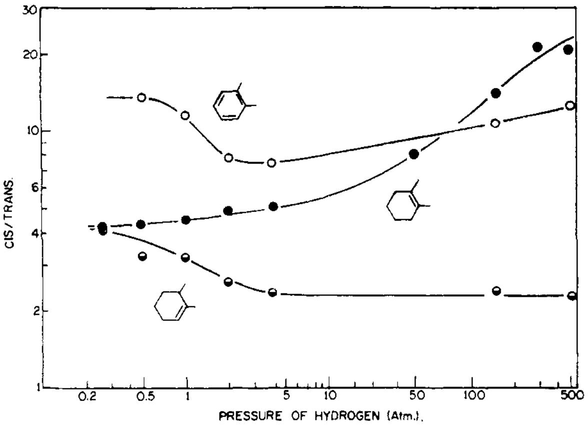


Fig. 1.—Hydrogenation of *o*-xylene and its tetrahydro derivatives on PtO_2.

The experimental procedures have been described previously.[10] Each experiment employed approximately the same quantities of reactants; 0.2 ml. of the substrate, 20 mg. of the catalyst and 5.0 ml. of glacial acetic acid. The products were isolated and analyzed by gas chromatography.

TABLE I

STEREOCHEMISTRY OF HYDROGENATION OF ALKYLTOLUENES ON PtO_2 AT 25°, ACETIC ACID SOLVENT

Pressure atm.	*cis*-Dialkylcyclohexane, %			
	o-CH_3–	*m*-CH_3–	*p*-CH_3–	*p*-*t*-C_4H_9
0.25	..	77	70	..
0.5	93	..	73	56
1	92	77	73	61
2	88	76	72	..
3	..	73	..	61
4	88	..	74	63
6	..	77	..	..
75	..	82	80	68
150	92	84	80	..
300	93	85	82	71

TABLE II

HYDROGENATION OF ALKYLTOLUENES, ESTIMATE OF MINIMUM FRACTION DESORBED AS DIALKYLCYCLOHEXENE

Alkyltoluene	Fraction desorbed as cycloalkene[a]	
	1 atm.	100 atm.
o-CH_3–	0.4–0.7	0.3–1.
m-CH_3–	.5–1.	.3–0.9
p-CH_3–	.5	.4
p-*t*-C_4H_9–	.6–0.8[b]	.6[b]

[a] The lower figure assumes that the only cycloalkene which is desorbed is that one which yields the smallest *cis*/*trans* ratio; the larger value is for the cycloalkene which experimentally yields the largest ratio. For the dimethylcyclohexenes, the relationship is 1,2- > 2,3- and 1,3- > 2,4-. 1,4-Dimethylcyclohexene is the only possible alkene derivative of *p*-xylene in which the relative configurations of the alkyl groups have not been fixed. [b] 1-Methyl-4-*tert*-butylcyclohexene; 4-methyl-1-*tert*-butylcyclohexene would be expected to yield approximately 50% *cis*.[11]

Results

Hydrogenation over reduced platinum oxide in acetic acid at *ca.* 25° converts the isomeric xylenes and *p*-*tert*-butyltoluene to a mixture of the *cis*- and *trans*-dialkylcyclohexanes. The *cis*/*trans* ratio drops in the series *o*-methyl- > *m*-methyl- > *p*-methyl- > *p*-*tert*-butyltoluene and, at pressures above one atmosphere, the ratios increase with increasing pressure. *o*-Xylene is exceptional at pressures below one atmosphere, the *cis*/*trans* ratio increasing with a *decrease* in pressure. With a single exception (1,2-dimethylcyclohexene compared to *o*-xylene at high pressures), the aromatic hydrocarbon yields more of the *cis* isomer than does any of the derivable cyclohexenes in which the final configuration (*cis* or *trans*) is not yet fixed, *e.g.*, one substituent is attached to the double bond. In Table II is presented an estimate of the fraction of the material which must pass through any one of these possible cycloalkenes, assuming it alone is desorbed during the reaction. The desorbed alkene is assumed to yield the same ratio of *cis*/*trans* isomers in the presence of its aromatic precursor as in its absence. The data for the cycloalkenes are recorded elsewhere[10,12] but for comparison with the aromatic hydrocarbons is presented graphically in Figs. 1, 2, 3 and 4.

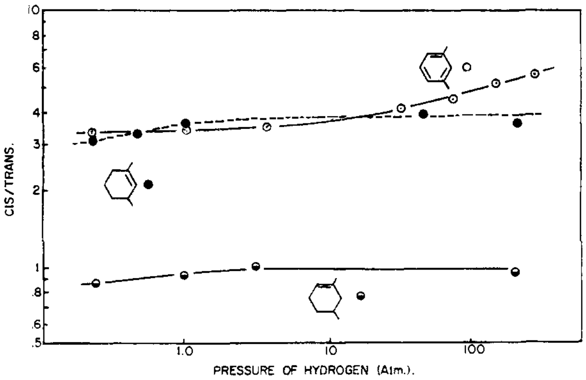


Fig. 2.—Hydrogenation of *m*-xylene and its tetrahydro derivatives on PtO_2.

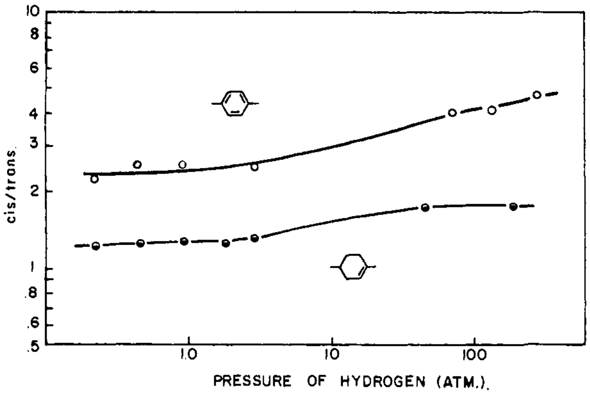


Fig. 3.—Hydrogenation of *p*-xylene and 1,4-dimethylcyclohexene on PtO_2.

Alternatively, one may calculate the percentage of *cis* isomer which would result if all of the substrate which has combined with four atoms of hydrogen is desorbed as an alkene, assuming that (1) the distribution of these isomeric alkenes is statistical, and (2) that the *cis*/*trans* ratio obtained from each is that which is observed in the absence of its aromatic precursor as above. For example, *o*-xylene should yield the following proportion of

---

[11] J. F. Sauvage, R. H. Baker and A. S. Hussey, *J. Am. Chem. Soc.*, **82**, 6090 (1960).

[12] S. Siegel, G. V. Smith, M. Dunkel and W. Halpern, unpublished research.

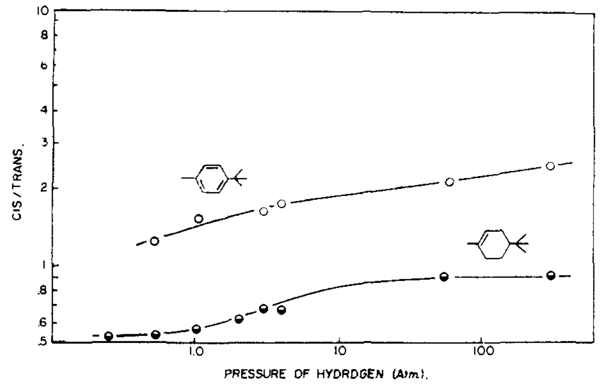


Fig. 4.—Hydrogenation of *p-tert*-butyltoluene and its tetrahydroderivatives on PtO_2.

cycloalkenes: 1,2-dimethylcyclohexene, 16.6%; 2,3-dimethylcyclohexene, 33.3%; *cis*-3,4-dimethylcyclohexene, 33.3%; and *cis*-4,5-dimethylcyclohexene, 16.6%. It is probable that the latter two would yield exclusively the *cis* saturated stereoisomer under the specified conditions.

Accordingly, one estimates the percentage of the *cis* isomer at 1 and 4 atmospheres as 90 and 87 while the observed values are 93 and 88, respectively. Similarly, at 1 atmosphere, *m*-xylene yields 77% *cis* (the estimated value is 74%) and for *p*-xylene the observed value is 73%, and calculated 71%. These values diverge more widely at high pressures of hydrogen, the aromatic hydrocarbon yielding more of the *cis* isomer than is estimated by this simple calculation. Representative estimates are given in Table III.

Table III

Percentage of *cis*-Dialkylcyclohexane Formed in Hydrogenation of Alkyltoluenes

Compd.	1 Atm.		100 Atm.	
	Calcd.	Obsd.	Calcd.	Obsd.
o-CH_3–	90	93	88	91
m-CH_3–	74	77	76	83
p-CH_3–	70	73	76	80
p-t-C_4H_9–	62[a]	61	70[a]	69

[a] Assuming 1-*tert*-butyl-4-methylcyclohexene yields the same proportion of *cis* isomer as is obtained from 1,4-dimethylcyclohexene; see ref. 11 for a justification of this assumption.

Discussion

The mechanism proposed by Horiuti and Polanyi[13] for the surface-catalyzed reaction of hydrogen with unsaturated compounds has found support from several lines of evidence.[14] In essence, it supposes that the reactants are adsorbed upon the surface, the hydrogen dissociatively, and further changes consist of a succession of transfers of hydrogen atoms between the surface and the carbon atoms attached to the surface, a displacement reaction which occurs with retention of configuration at the carbon atom, or the reverse of any of these steps.

The hydrogenation of the benzene ring in *o*-xylene may be represented according to this mechanism, as in Fig. 5. In principle, any of the intermediates represented as adsorbed species might desorb from the surface, but since this dissociation is endothermic, only the more stable compounds, such as a cycloalkene, are likely to leave the surface before the last stage in the reduction has been reached. Indeed, to account for the fact that *trans*-dimethylcyclohexane is one of the products, 2,3-dimethylcyclohexene must desorb and readsorb on the opposite face of its double bond. As the pressure of hydrogen is increased, the reactions requiring hydrogen will be accelerated relative to the reverse processes and the chance that an unsaturated molecule will be desorbed is diminished. Consequently, more of the *cis* isomer, compared to the *trans* isomer, will be formed as the pressure of hydrogen is increased.

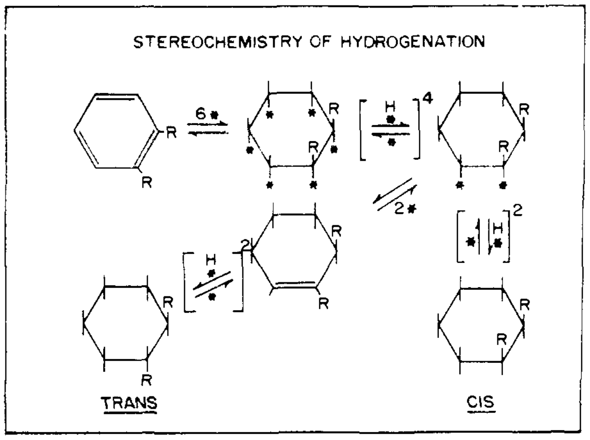


Fig. 5.

One may question whether a desorbed cyclohexene which escapes detection is a reasonable intermediate in the hydrogenation of an aromatic ring. Balandin once suggested, in consideration of his "multiplet" theory of catalysis,[15] that the addition of the six hydrogen atoms are simultaneous, although he has since modified his views.[16] Recently, however, Madden and Kemball observed cyclohexene during the early stages of the vapor phase hydrogenation (flow system) of benzene over nickel films at 0 to 50°.[17] The ratio of cyclohexene to cyclohexane diminished with time and little or none of the alkene was detected if the films were annealed at 50° in a stream of hydrogen.

Elsewhere we have observed the formation of *o*-xylene during the hydrogenation of 1,2-dimethylcyclohexene[10] under reaction conditions identical (except for the substrates) with those in the reduction of *o*-xylene. Thus, a reaction path joining *o*-xylene to the 1,2-dimethylcyclohexene to the saturated isomers is demonstrated. Because the alkene is more rapidly reduced under these conditions than the aromatic compound,[18] the former is not readily observed.

Although the formation of the *trans*-dialkylcycloalkanes can be accounted for by a mechanism

---

[13] I. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

[14] T. I. Taylor, "Catalysis," Vol. V, edited by P. H. Emmett, Reinhold Publishing Corp., New York, N. Y., 1957, chapter 5.

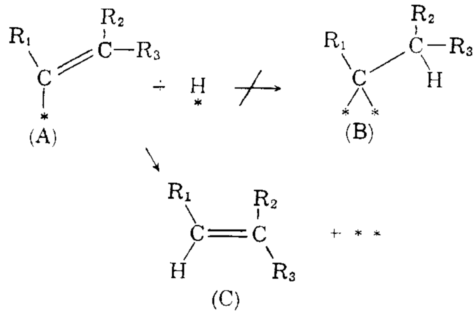
[15] A. A. Balandin, *Z. physik. Chem.*, **B2**, 289 (1924).

[16] A. A. Balandin, "Advances in Catalysis," Vol. X, Academic Press, Inc., New York, N. Y., 1958, p. 96.

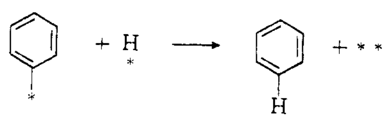
[17] W. F. Madden and C. Kemball, *J. Chem. Soc.*, 302 (1961).

[18] H. A. Smith and H. T. Meriwether, *J. Am. Chem. Soc.*, **71**, 413 (1949).

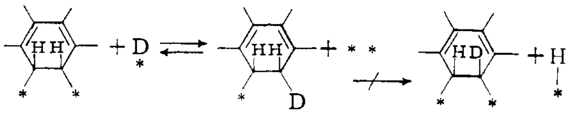
which requires the desorption of a cycloalkene, it might be formed *via* some surface complex (A) such as one postulated by Burwell[19] to explain the racemization of an optically active alkane while undergoing exchange with deuterium atoms on the catalytically active surfaces of noble metals. However, as discussed elsewhere,[3] the most probable reaction of this intermediate with hydrogen is one yielding an alkene (C) rather than another surface complex (B).



Further, the experiments of Anderson and Kemball on the deuteration of benzene[20] indicated that the exchange with benzene involved chemisorbed phenyl and phenylene radicals while the addition proceeded in a parallel reaction which involved little or no additional exchange with deuterium. Such a mechanism was first postulated by Farkas and Farkas.[21] The geometrical relationship of the phenyl radical to the surface atoms should be analogous to the intermediate A and apparently the preferred reaction path with hydrogen is the abstraction of hydrogen from the surface to release a molecule of benzene.



Stereochemical arguments support the view that the exchange of hydrogen in benzene proceeds *via* the dissociative mechanism. The rival associative mechanism[13] fails for the reasons cited by Burwell in explaining why neither dissociative adsorption of an alkane nor the migration of the point of attachment to the surface of the half-hydrogenated state could account for the racemization of an optically active saturated hydrocarbon.[19] The replacement of a carbon to surface bond by a carbon to hydrogen bond occurs with retention of configuration at the carbon atom, and the reverse process must do likewise to be consistent with the principle of microscopic reversibility. Indeed, if the associative mechanism were operative for the exchange, then either di- or tetradeuteriobenzene should be more abundant than monodeuteriobenzene[21] because only *via* the desorption and readsorption, on its opposite face, of either cyclohexadiene or cyclohexene followed by dehydrogenation to benzene could the hydrogen be exchanged for deuterium in accord with the stereochemical restrictions of the postulated scheme.[22]



The associative mechanism for the *addition* of hydrogen to the benzene ring is supported by the observed stereochemistry of the hydrogenation of aromatic compounds and related cyclohexenes. It is not certain that every molecule of the cycloalkane which is formed passes through a desorbed cycloalkene, although a considerable portion must. But the fraction which does so is apparently a function of the pressure of hydrogen.

Acknowledgment.—The support by a grant from the National Science Foundation is gratefully acknowledged. This research was also supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

---

(19) R. L. Burwell, Jr., *Chem. Revs.*, **57**, 895 (1957).

(20) J. R. Anderson and C. Kemball, in ref. 7, p. 51.

(21) A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **33**, 827 (1937).

(22) R. L. Burwell, Jr., in ref. 7, p. 87.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS.]

The Synthesis of Certain Azabicyclic Ketones[1a]

BY HERBERT O. HOUSE, PETER P. WICKHAM[1b] AND HANSPETER C. MÜLLER

RECEIVED MARCH 15, 1962

The N-methyl derivatives of 3-azabicyclo[3.2.1]octan-8-one, 3-azabicyclo[3.3.1]nonan 9-one and 8-azabicyclo[4.3.1]-decan-10-one have been prepared by the direct reaction of methylamine and formaldehyde with cyclopentanone, cyclohexanone and cycloheptanone, respectively. The azabicyclooöctanone also was obtained by a multi-step reaction sequence.

As substrates for a study of conformation, the stereodirective influence of an amine function on addition reactions and the stereochemistry of N-alkylation, we desired synthetic routes to the azabicyclic ketones **1**, **2** and **3**. Although the derivative **4** had been described[2] previously and the derivative **5** was described[3] during the course of

---

[1] (a) This research is supported by grants from the Alfred P. Sloan Foundation, the National Institutes of Health (RG-8761) and the McNeil Laboratories, Inc. (b) National Institutes of Health Predoctoral Fellow, 1958–1960.

(2) E. F. L. J. Anet, G. K. Hughes, D. Marmion and E. Ritchie, *Austral. J. Sci. Research*, **3A**, 330 (1950).

(3) F. F. Blicke and F. J. McCarty, *J. Org. Chem.*, **24**, 1379 (1959).