Relative Rates and Products from Pyrolysis of Alkyl-Substituted *gem*-Dichlorocyclopropanes

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Relative pyrolytic reactivities in the alkyl-substituted *gem*-dichlorocyclopropanes decrease in the sequence 2,2,3,3-$(CH_3)_4$ > *cis*-2-C_2H_5-3-CH_3 > 2,2-$(CH_3)_2$ > *trans*-2-C_2H_5-3-CH_3 > 2,3-$(CH_2)_4$ > *n*-C_4H_9 > CH_3 > H in agreement with the sequence predicted by a quasi-ionic isomerization to an allylic cation from a cyclopropyl cation. The products formed are consistent with this hypothesis.

The ready availability of *gem*-dichlorocyclopropanes from the dichlorocyclopropanation[1] of olefins has prompted us to explore synthetic uses for these materials. In this paper we report a study of the reaction products from vapor phase pyrolysis (nitrogen carrier gas) over a calcium oxide substrate[2] of a variety of simple alkyl-substituted *gem*-dichlorocyclopropanes. Incidental to this study we have accumulated data on relative reactivities of these materials. These results considered together with a recent quantitative study on pyrolysis of chlorocyclopropane[3] give an insight into the mechanism of *gem*-dichlorocyclopropane pyrolysis.

Experimental Section[4]

Materials.—*gem*-Dichlorocyclopropanes were prepared by dichlorocyclopropanation of the corresponding olefin in tetraglyme with sodium hydroxide and chloroform[1b] with final purification by distillation (55-cm spinning band column) monitored by vpc. These included 1,1-dichlorocyclopropane (bp 75.5–76°, lit.[5] bp 75°), 1,1-dichloro-2-methylcyclopropane (bp 102°), 1,1-dichloro-2,2-dimethylcyclopropane (bp 118°, lit.[6] bp 119–120°), 1,1-dichloro-2-*n*-butylcyclopropane (bp 83–84° (40 mm), lit.[6] bp 75–76° (25 mm), *cis*-1,2-dichloro-2-methyl-3-ethylcyclopropane (bp 69–70° (50 mm), lit.[7] bp 64–68° (49 mm)), 1,1-dichloro-2,2,3,3-tetramethylcyclopropane (mp 50.5–51.5°, lit.[7] mp 49.8–50.5°), and 7,7-dichlorobicyclo[4.1.0]heptane[8] (identical by vpc with authentic material). The calcium oxide was from freshly opened bottles and was protected from air when not in use.

Pyrolysis Procedure.—The pyrolysis apparatus was similar to one described previously.[2] The pyrolysis column was packed with lump calcium oxide (116 g, 2.07 moles) and the reaction temperature was measured by a thermocouple in a Pyrex tube within the calcium oxide packing.[9] The material to be pyrolyzed was added dropwise onto the heated calcium oxide using a stream of nitrogen (190 cc/min unless otherwise specified) to regulate contact time and sweep the pyrolysate into a Dry Ice–acetone-cooled U-tube where it was condensed. The free volume of the packed section of the pyrolysis tube was 85 ml which at the normal nitrogen flow rate gave a residence time in seconds of $8050/T$ (T in °K). All comparative pyrolysis rates were measured with a single calcium oxide charge and in no case was hydrogen chloride detected in the exit gases. Some losses of the more volatile materials occurred owing to the high carrier gas throughput. Carbonization on the column also occurred at very high temperatures (above 460°, 10-sec contact time).

Relative Pyrolysis Rates.—Typically, equal weights (usually 1 g) of the *gem*-dichlorocyclopropanes to be studied were mixed, examined by vpc, and subjected to pyrolysis. The pyrolysate was weighed and examined again by vpc. Where pyrolysis products obscured the starting material peaks a dilute *n*-hexane solution of a portion of the pyrolysate was repeatedly extracted with concentrated sulfuric acid. This removed the unsaturated pyrolysis products permitting determination of unreacted starting material. It was verified, where necessary, that the starting *gem*-dichlorocyclopropanes were unaffected by this treatment. Comparison of the original and final vpc traces showed which material pyrolyzed most rapidly. The temperature required for substantial pyrolysis was also noted. Relative reactivities were calculated as the quotient of the relative peak heights of the two components after and before pyrolysis. The most likely source of error is some differential loss of the more volatile *gem*-dichlorocyclopropane.

Pyrolysis of 1,1-dichlorocyclopropane (3.03 g) was studied at five temperatures (Table I). The major pyrolysis product was 2,3-dichloropropene (identified by vpc comparison with an authentic sample) with two unidentified low-boiling products also being formed at very high temperatures.

TABLE I

Temp, °C	Pyrolysate, g	Rel area, % Starting material	2,3-Dichloropropene
404–405	2.30	100	0
423	2.34	93	7
435–438	2.38	89	11
457–475	1.70	60	40
465–472	1.05	47	53

Pyrolysis of 1,1-dichloro-2-methylcyclopropane (2.76 g) was studied at several temperatures and nitrogen flow rates (results are given in Table II). Major products included chloroprene, 2,3-dichlorobutene-1, and 1,2-dichlorobutene-2.

TABLE II

			Area, %			
N_2 flow, cc/min	Temp, °C	Pyrolysate, g	Starting Material	Chloroprene	2,3-Dichlorobutene-1	1,2-Dichlorobutene-2
240	464–466	0				
240	432–434	0.8		Trace		
240	414–425	1.21	Trace	Trace	Trace	Trace
475	420–426	0.93	24	31	11	16
240	405–408	2.08	39	16	22	22
475	309–402	1.31	65	8	15	10
190	408–411	2.19	34	16	26	21

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[1] (a) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964, pp 145–147; (b) G. C. Robinson, *Tetrahedron Letters*, 1749 (1965).

[2] Previous work on pyrolysis of 7,7-dichlorobicyclo[4.1.0]heptane indicates that hydrogen chloride formed during pyrolysis may catalyze product-altering side reactions: G. C. Robinson, *J. Org. Chem.*, **29**, 3433 (1964).

[3] (a) R. C. S. Grant and E. S. Swinbourne, *Chem. Comm.*, 620 (1966). (b) It should be noted that these workers used a glass static system and the present work used a calcium oxide packed flow system. It is believed that chlorocyclopropanes are inert to calcium oxide under the pyrolysis conditions but this has not been rigorously proven.

[4] A standard vpc column 10% Carbowax 20M on Chromosorb P (15 ft by 0.25 in.) was used; nmr spectra were taken in parts per million relative to tetramethylsilane (Varian A-60 spectrometer) with coupling constants in cycles per second. Boiling points and melting points are uncorrected.

[5] M. T. Rodgers and J. D. Roberts, *J. Am. Chem. Soc.*, **68**, 843 (1946).

[6] W. von E. Doering and A. K. Hoffman, *ibid.*, **76**, 6162 (1954).

[7] (a) W. von E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958). (b) A mixture of *cis* and *trans*-1,1-dichloro-2-ethyl-3-methylcyclopropane was prepared from mixed *cis*- and *trans*-pentene-2 by the standard procedure and used as a source of the *trans* isomer since *trans*-pentene-2 was not readily available.

[8] W. M. Wagner, H. Kloosterziel, and S. van der Ven, *Rec. Trav. Chim.*, **80**, 740 (1961).

[9] In ref 2 temperature was measured at the furnace–pyrolysis tube annular space where temperature runs higher than within the tube.

Chloroprene was identified by vpc comparison with authentic material and by its infrared spectrum. The dichlorobutenes were isolated in fair purity by careful distillation, and pure samples for nmr examination were separated by preparative vpc. The lower boiling material was 2,3-dichlorobutene-1: bp 112° (lit.[10] 110–111°); infrared bands, 1634 and 873 (vinylidene olefin) and 1376 cm^{-1} (methyl attached to carbon); nmr (deuteriochloroform) at 1.66 (three-proton methyl doublet, coupled to the adjacent proton, $J = 6.8$ cps), at 4.64 (allylic proton multiplet), at 5.20 (vinyl proton *trans* to chlorine, coupling to *cis* proton $J = 1.9$ cps, coupling to *trans* allylic proton $J \leq 0.4$ cps), and at 5.52 ppm (vinyl proton *cis* to chlorine, coupling to allylic proton, $J = 0.6$ cps). The higher boiling material was 1,2-dichlorobutene-2: bp 128° (lit.[10] bp 130–131°); infrared bands, 1661 (internal olefin), 816 (trisubstituted olefin CH out-of-plane bending), and 1376 cm^{-1} (methyl attached to carbon); nmr (deuteriochloroform) 1.76 (allylic methyl doublet coupled to adjacent vinyl H, $J = 6.8$ cps, further coupled to allylic CH_2, $J = 0.9$ cps), 4.16 (allylic CH_2 multiplet), and 5.98 ppm (vinyl H coupled to adjacent methyl and to *cis* methylene, $J = 0.7$ cps).

Pyrolysis of 1,1-dichloro-2,2-dimethylcyclopropane at three temperatures gave (by vpc) only 2-chloro-3-methylbutadiene: bp 91–101° (lit.[11] bp 93°); infrared bands 1590 (conjugated C=C with overtone at 3300), 880 (vinylidene olefin), 1370 (methyl bonded to carbon), 825 (C–Cl), and 3100 cm^{-1} (vinyl CH). Total infrared spectrum substantially identical with the standard reference spectrum. The temperatures and yields were 438 ± 7° (62%), 454 ± 4° (57%), and 494 ± 6° (8%).

Pyrolysis of 1,1-dichloro-2,2,3,3-tetramethylcyclopropane (428° measured at the pyrolysis tube-furnace annular space) gave only 2,4-dimethyl-3-chloropentadiene-1,3: bp 58° (65 mm); 46% yield); ultraviolet spectrum λ_{max} 234 mμ (ε 1900); infrared spectrum, 590 (C–Cl), 1638 (C=C), 1370 ($C–CH_3$), 893 ($C=CH_2$), 3096, 2985, 2933, 2865, 995, and 906 cm^{-1}; nmr (deuteriochloroform) 4.87 (complex), 5.04 (complex), 1.86 (methyl singlet, intensity 2), and 1.80 ppm (methyl doublet, intensity 1); hydrogen uptake 5.84 moles/mole (expected 6.0 moles/mole).[12]

Pyrolysis of *cis*-1,1-dichloro-2-ethyl-3-methylcyclopropane was studied at several temperatures (Table III). The two major pyrolysis products, both of lower retention time than the starting material, were isolated by preparative vpc.[13] One was 3-chlorohexadiene-1,3; it had infrared bands at 971 and 907 (vinyl out-of-plane bending modified by conjugation), 840 (trisubstituted olefin), 1402 (allylic methylene), 1640 and 1608 (conjugated double bonds, doublet due to *cis,trans* isomers or chlorine substitution), 1825 (overtone 907 band), and 1176 cm^{-1} (not assigned); nmr signals appeared at (five alkyl and four vinyl protons) 6.4 (quadruplet, proton at carbon 2), 5.33 (multiplet, two vinylidene protons), 5.77 (triplet, proton at carbon 4), 2.30 (methylene multiplet), and 1.02 ppm (methyl triplet). The second product was 3-chlorohexadiene-2,4 which had infrared bands at 1623 (conjugated diene), 1376 ($C–CH_3$), 952 (butadiene band), 823 (trisubstituted olefin), 771 (carbon–chlorine), 1180 (not assigned), 1960, 1852, 1805, 1776, and 1725 cm^{-1} (overtones); nmr (alkyl to vinyl proton ratio 2.07, calcd 2.0) signals appeared at 1.8 (asymmetric triplet, overlapping methyl doublets), 6.05 (AB pattern of adjacent vinyl protons), and 5.65 ppm (quartet, lone vinyl proton).

Table III

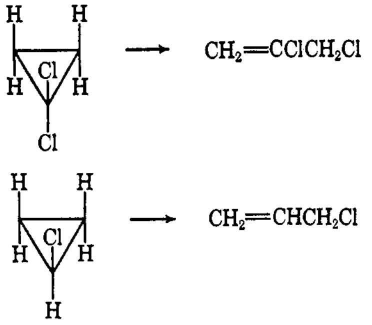
Temp, °C	Charged, g	Recovered, g	Unreacted, area % product
331–333	1.26	0.86	0
318–321	1.05	0.70	0
287–289	1.05	0.69	Trace
265–267	1.05	0.75	25
283–289	5.25	4.02	Trace

Pyrolysis of 1,1-dichloro-2-*n*-butylcyclopropane (2.54 g at 407–416°) gave a pyrolysate (1.6 g) with four major components having vpc retention times less than starting material and two of longer retention time. The products were not studied further.

Results and Conclusions

1,1-Dichlorocyclopropane was stable under the standard conditions at 404–405° (11.9-sec contact time) but 7% conversion to 2,3-dichloropropene was noted at 423° (11.6-sec contact time). As the pyrolysis temperature was increased two unidentified additional products boiling below 25° were formed and higher conversions were obtained. The 1,1-dichlorocyclopropane was half-converted at about 460° (11-sec half-life).

Comparison of the above results with those of Grant and Swinbourne on pyrolysis of chlorocyclopropane suggests similar mechanisms of pyrolysis.



In each case the product seems to result from cleavage of the cyclopropane ring opposite the chlorine-bearing ring carbon with double-bond formation accompanied by chlorine migration to an allylic site. As was observed by Swinbourne and Grant, the rearrangement is far more facile than in alkylcyclopropane isomerization[14] to olefins suggesting that hydrogen migration in a diradical species is not involved. The most stable diradical would form by cleavage at the chlorine-substituted carbon atom,[15] not at the opposite bond where cleavage actually occurred. Assuming the present pyrolysis of 1,1-dichlorocyclopropane to be homogeneous and first order as was verified for chlorocyclopropane, one finds $k_1 = 0.01$ sec^{-1} (chlorocyclopropane) and $k_1 = 0.06$ sec^{-1} (1,1-dichlorocyclopropane) at 460°. The similar rates suggest 1,1-dichlorocyclopropane does in fact rearrange by a homogeneous first-order process. Detailed discussion of the rearrangement process will be deferred until the effect of substitution and stereochemistry on products and relative reaction rates has been presented.

Pyrolysis of 1,1-dichloro-2-methylcyclopropane (Ia) occurred at a lower temperature than pyrolysis of the parent 1,1-dichlorocyclopropane. At 405° where 1,1-dichlorocyclopropane was stable for more than 12 sec Ia was 60% rearranged in 9 sec. The major products were chloroprene (IVa), 2,3-dichlorobutene-1 (IIa), and 1,2-dichlorobutene-2 (IIIa). The identification of IVa was by its infrared spectrum and by vpc comparison with authentic material while IIa and IIIa were identified from their boiling points and their infrared and nmr spectra. The dichlorobutenes are allylic isomers

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[10] J. H. Blumbergs, Belgian Patent 617,557 (Aug 1962).

[11] W. H. Carothers and D. D. Coffman, *J. Am. Chem. Soc.*, **54**, 4071 (1932).

[12] H. C. Brown and C. A. Brown, *ibid.*, **84**, 2829 (1962). Two hydrogen atoms are required for saturation of each of the two double bonds and for cleavage of the carbon to chlorine bond.

[13] A mixture of *cis*- and *trans*-1,1-dichloro-2-ethyl-3-methylcyclopropane, prepared by dichlorocyclopropanation of mixed *cis*- and *trans*-pentene-2 gave a similar product mixture on pyrolysis at 347° where both isomers are extensively reacted.

[14] H. M. Frey, *Advan. Phys. Org. Chem.*, **4**, 147 (1966).

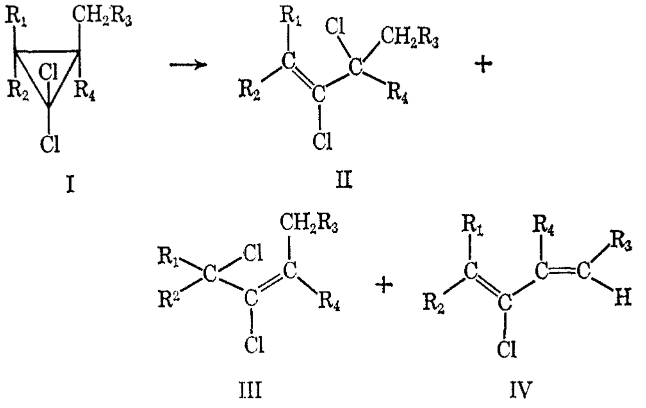
[15] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 50.

TABLE IV

RELATIVE PYROLYTIC REACTIVITIES OF *gem*-DICHLOROCYCLOPROPANES[a]

Substituents I[b]	Substituents II	Temp, °C	Recovery, g/g charged	Estimated half-lives of I	Rel reactivity[c]
	CH_3	461–466	0.50	0.5	0.016[d]
CH_3	*n*-C_4H_9	395–404	0.55	0.5[e]	0.60[d]
n-C_4H_9	2,3-$(CH_2)_4$	395–399	0.55	3	0.40
CH_3	2,3-$(CH_2)_4$	391–393	0.62	3–4	0.09
2,3-$(CH_2)_4$	2,2-$(CH_3)_2$	378–380	0.56	3	0.06
2,3-$(CH_2)_4$	2,2-$(CH_3)_2$	365–367	0.61	1	0.33
trans-2-C_2H_5-3-CH_3	*cis*-2-C_2H_5-3-CH_3	347	0.75		0.12[f,g]
trans-2-C_2H_5-3-CH_3	2,2-$(CH_3)_2$	345–349	0.71		0.62[f,g]
2,3-$(CH_2)_4$	*trans*-2-C_2H_5-3-CH_3	349–354	0.62		0.76[f,g]
cis-2-C_2H_5-3-CH_3	2,2,3,3-$(CH_3)_4$	262–263	0.72	4	0.47
2,2-$(CH_3)_2$	2,2,3,3-$(CH_3)_4$	346–348	0.72		0.10[f]

[a] CaO packing, N_2 carrier. [b] Least reactive component. [c] (II–I)/(II–I)$_0$ from vpc analysis. [d] Upper limit due to possible losses of most volatile component. [e] Estimated from data on neat material. [f] Sulfuric acid extraction of pyrolysis products needed. [g] A mixture of *cis*- and *trans*-1,1-dichloro-2-methyl-3-ethylcyclopropane was used as a source of *trans* isomer.



a, $R_1 = R_2 = R_3 = R_4 = H$
b, $R_1 = R_2 = R_4 = H$; $R_3 = n\text{-}C_3H_7$
c, $R_1 = R_2 = R_3 = H$; $R_4 = CH_3$
d, $R_3 = H$; $R_1 = R_2 = R_4 = CH_3$
e, $R_2 = R_4 = H$; $R_1 = R_3 = CH_3$
f, $R_1 = R_3 = R_4 = H$; $R_2 = C_2H_5$

and both can arise from cleavage of the bond opposite the chlorine-substituted carbon in the cyclopropane ring with chlorine migration to an adjacent carbon atom. Dehydrohalogenation of either IIa or IIIa[16,17] can give IVa, but there is no direct evidence for the origin of IVa and it may arise directly in the pyrolysis.

The closely related material, 1,1-dichloro-2-*n*-butylcyclopropane (Ib) also pyrolyzed near 405°. The product mixture was complex showing six major components, two of longer retention time than starting material and four of shorter retention time. The products were not further investigated but are probably analogous to those from Ia pyrolysis.

Pyrolysis of 1,1-dichloro-2,2-dimethylcyclopropane (Ic) gave as sole product 2-chloro-3-methylbutadiene (IVc) while pyrolysis of 1,1-dichloro-2,2,3,3-tetramethylcyclopropane (Id) gave only 2,4-dimethyl-3-chloropentadiene-1,3 (IVd). The latter product has also been reported by Engelsma[18] from pyrolysis of Id. No dichloroolefin was detected in either case but the pyrolyses were at temperatures where the expected dichloro olefins (IIc, IId and IIIc, IIId) may be unstable.

Pyrolysis of *cis*-1,1-dichloro-2-ethyl-3-methylcyclopropane was rapid at 265° (15-sec residence time) giving 80% reaction. At 287° the pyrolysis was substantially complete giving two major pyrolysis products, 3-chlorohexadiene-1,3 (IVf) and 3-chlorohexadiene-2,4 (IVe), isolated by preparative vpc and identified by their infrared and nmr spectra. In spite of the mild reaction conditions no dichloro olefin (simple isomerization product) was found.[19] It should be noted that the stereochemistry of the products is still uncertain. It is known that the closely related hydrocarbon *cis*-hexadiene-1,3 isomerizes to *cis,trans*-hexadiene-2,4 with a half-life of 40 sec at 287°.[20] It seems doubtful that such isomerization processes are substantially affecting the product distributions observed here since the total reaction times are 14 sec, although the possibility cannot be ruled out entirely.

Although residence time differences and temperature fluctuations make determinations of absolute rate constants in the flow reactor used in this work of low precision, passage of substituted *gem*-dichlorocyclopropanes two at a time through the reactor with measurement of unreacted starting materials does give qualitative orders of pyrolytic reactivity, provided of course the materials all react by the same mechanism. In Table IV are given relative reactivities defined as the quotient of the final and initial ratio of the two substances charged along with the temperature, material recovery, and the approximate number of half-lives of the least reactive component. These relative reactivities are related only indirectly to the relative rates since the relative reactivity number is a decreasing function of the extent of reaction. However, use of the estimated half-lives of the least reactive material can give an approximation to the difference in reaction rates. For example, the first entry with a minimum reactivity of 1,1-dichloro-2-methylcyclopropane of 0.016 relative to 1,1-dichlorocyclopropane together with the value 0.5 half-lives of 1,1-dichlorocyclopropane suggests a factor of about six in the ratio of rate constants near 460°. Similarly one can estimate a two times greater pyrolysis rate for 1,1-dichloro-2-*n*-butylcyclopropane than for 1,1-dichloro-2-methylcyclopropane at 400°.

On a qualitative basis one can infer from the table a sequence of increasing thermal stabilities of substituted dichlorocyclopropanes: 2,2,3,3-$(CH_3)_4$ < *cis*-2-C_2H_5-3-CH_3 < 2,2-$(CH_3)_2$ < *trans*-2-C_2H_5-3-CH_3 < 2,3-

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[16] G. W. Hearne and M. L. Adams, U. S. Patent 2,391,827 (Dec 1945).

[17] H. P. Crocker, British Patent 825,609 (Dec 1959).

[18] J. W. Engelsma, *Rec. Trav. Chim.*, **84**, 187 (1965).

[19] Rearrangement of 1,1-dibromo-*cis*-2,3-dimethylcyclopropane in kerosene solution at 145–165° gave initially 3,4-dibromopentene-2: D. C. Duffey, J. P. Minyard, and R. H. Lane, *J. Org. Chem.*, **31**, 3865 (1966).

[20] H. M. Frey and B. M. Pope, *J. Chem. Soc., Sect. A*, 1701 (1966).

$(CH_2)_4 < n\text{-}C_4H_9 < CH_3 < H$. 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.

[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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[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.