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Kinetics of the Hydrogen Transfer Reaction of Cyclohexene on Palladium Powder

S. CARRÀ, P. BELTRAME, AND V. RAGAINI

From the Istituto di Chimica fisica, Università di Milano, Italy

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The disproportionation of cyclohexene to cyclohexane and benzene has been kinetically followed in tetrahydrofuran solution on palladium powder at 50° to 60°C. The behavior of 1,3-cyclohexadiene under the same conditions has been studied too. Gas chromatography was used for the analytical determinations. The diene is noticeably more reactive than cyclohexene, and has been detected in low concentration in the reaction products from the latter. It is suggested that it is an intermediate of the reaction.

Experimental results of the kinetics of cyclohexene are well accounted for by a second order rate law that takes into account the adsorption of cyclohexene and benzene on the catalyst. The adsorption coefficients for benzene are ca. five times larger than those of cyclohexene. Adsorption heats are 5.2 and 9.3 kcal/mole, respectively, for cyclohexene and benzene from the solution. The activation energy of the reaction is 14 kcal/mole.

Details are given of the application of the steepest descent method for the least-squares fitting of the kinetic equation to experimental data.

INTRODUCTION

The disproportionation of cyclohexene to benzene and cyclohexane on palladium catalysts has been studied by Zelinsky and Pavlov (*1*), and more recently in the gas phase by Gryaznov, Yagodovskii, and co-workers (*2*). Linstead, Braude, and Mitchell (*3*) studied this reaction in tetrahydrofuran (THF) solution at 65°C on palladium black, and also examined the behavior of 1,3-cyclohexadiene under the same conditions. These authors found a half-life for cyclohexene about twice that of the diene and during the reaction of the former did not find more than 1% of cyclohexadiene in the solution. From these results they suggested as probable a termolecular reaction of cyclohexene on the catalyst in which two molecules of the olefin act as acceptor of hydrogen donated by the third one. A more detailed kinetic investigation in THF solution with palladium powder as catalyst seemed of interest to us in order to improve the knowledge of the reaction mechanism.

EXPERIMENTAL

Materials. Cyclohexene was prepared from cyclohexanol by standard phosphoric acid dehydration (*4*), followed by distillation in a Todt column. 1,3-Cyclohexadiene was obtained by bromination of cyclohexene and successive dehydrobromination with sodium ethoxide in ethanol according to Mousseron and Winternitz (*5*). The product was distilled, washed with a large amount of water, and separated by centrifugation. The purity of both products was checked by gas chromatography. The THF was a B.D.H. product. Benzene was an RS (special reagent for cryoscopy) C. Erba product. The catalyst was precipitated by bubbling ethylene through a 0.05–0.08 *M* $PdCl_2$ aqueous solution. The palladium powder was washed by decantation a few times with acetone and then exhaustively with distilled water, and dried in an oven at 100°C. All kinetic runs, except where specified, have been performed with catalyst from the same batch.

Apparatus and procedure. The batch reactor was a cylindrical glass vessel (about

500 ml capacity) equipped with an efficient stirrer (1500 ± 50 rpm), a reflux condenser, and a microsyringe for analytical sampling. The vessel was immersed in a thermostated bath; the temperature of the reaction mixture was constant ± 0.1°C. The typical run was conducted on a 2.073 *M* cyclohexene solution in THF (about 125 ml) containing 100 to 400 mg of palladium catalyst. Ten 0.1–0.2 ml samples were ordinarily taken, at regular intervals during 3 to 5 hr, and immediately analyzed. In some runs benzene was introduced in the initial solution, substituting a few milliliters of it for the same volume of THF.

A few experiments were conducted on cyclohexadiene (0.920 *M* in the THF) under conditions similar to the typical run on cyclohexene, but on a lesser amount of solution (about 55 ml).

Analytical method. The gas-chromatographic analyses were performed on a "Fractovap B/f" (C. Erba) using a 3-meter stainless steel column of 20% Carbowax 400 on 30–60 mesh Celite at 95°C. Hydrogen was used as the carrier gas. Pure samples of the compounds under examination were mixed in known proportions (about the same met during the analyses) and peaks areas were calibrated. Under constant gas-flow conditions the following retention times and molar calibration factors (in parentheses) were found: cyclohexane, 3 min (0.84); cyclohexene, 4.5 min (0.93); cyclohexadiene, 6.5 min (1.00); THF, 8 min (1.02); benzene, 10 min (1.00).

The concentration of every compound in each run was evaluated from corrected peaks areas through a normalization factor, easily determined as the reaction proceeds without change of the total mole concentration.

Results

Runs on Cyclohexene

Reactions were carried out at 50.3°, 55.3°, and 60.5°C with four runs at each temperature, variable amounts of palladium

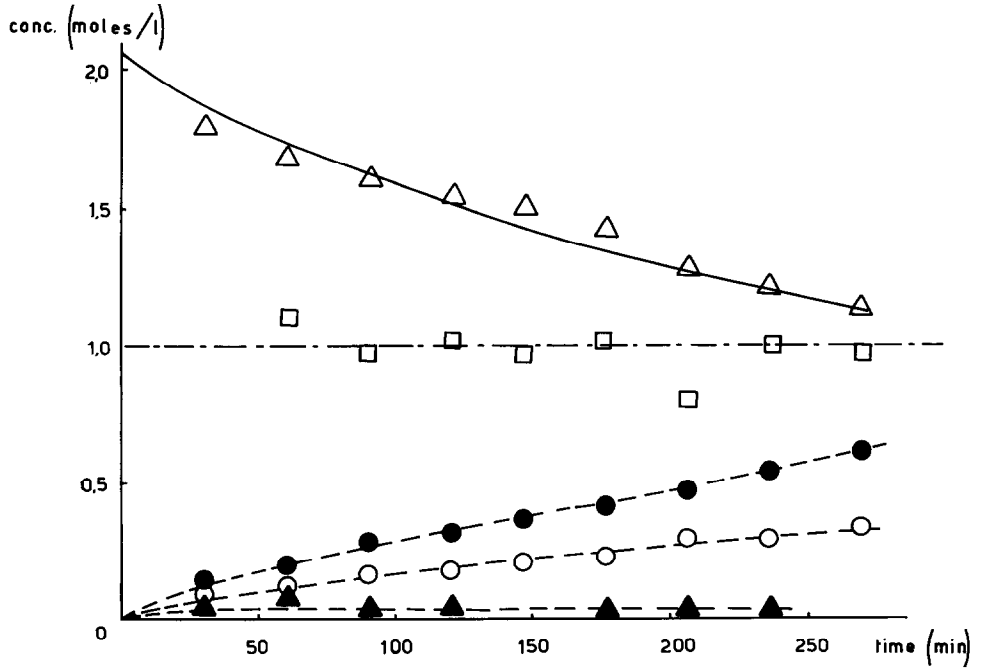


FIG. 1. Reaction of 2.073 *M* cyclohexene in THF (ca. 125 ml) on 300 mg Pd at 50.3°C: △, cyclohexene; ●, cyclohexane; ○, benzene; ▲, cyclohexadiene; □, values of R (= cyclohexane/2 × benzene). The solid line is calculated from Eq. (5). Dotted lines are simply drawn through the experimental points.

at the same (2.073 M) initial concentration of cyclohexene being used. The results of an experiment at 50.3°C are shown in Fig. 1, where concentrations of cyclohexene, cyclohexane, benzene, and cyclohexadiene are reported vs reaction time, together with values of the ratio R defined as:

$$R = \frac{[C_6H_{12}]_t - [C_6H_{12}]_{t_1}}{2([C_6H_6]_t - [C_6H_6]_{t_1})}$$

where t_1 = time corresponding to the first sample. In the various experiments the values of R were near to unity; the average values at 50.3, 55.3, and 60.5°C were found to be, respectively, 0.94, 0.98, 0.96. Therefore the stoichiometry of the observed reaction is close to the theoretical for

$$3C_6H_{10} \rightarrow 2C_6H_{12} + C_6H_6 \qquad (1)$$

In several runs cyclohexadiene was detected in lesser amounts than in the experiment shown in Fig. 1, so as to make difficult a quantitative evaluation, but no difference was observed in kinetic behavior.

The kinetic treatment of the results was based on the decrease of cyclohexene concentration. Examples are given in Fig. 2.

Some further runs were conducted, introducing different amounts of benzene in the initial solutions in order to investigate the influence of its adsorption on the kinetics. The results are shown in Fig. 3. (They are not exactly consistent with the previous ones because the catalyst prepared in a separate batch was less active.)

Runs on Cyclohexadiene

Five runs have been performed on THF solutions of cyclohexadiene (initial conc. = 0.920 M) at the previously mentioned temperatures, for a comparison of reactivities. An example is given in Fig. 4.

For a quantitative evaluation of the different reactivities of cyclohexadiene and cyclohexene, first order rate constants k_1 were calculated from the (roughly linear) plots of ($\ln c^\circ/c$) vs time where c° is the initial concentration of the reagent under consideration and c its concentration at time t. In the calculation of k_1 for the decomposition of the cyclohexene formed from cyclohexadiene, a time was chosen as "zero" at which the cyclohexadiene concentration had fallen to a small and nearly constant value (51 min in the example of Fig. 4). Such a procedure seemed justified by the large difference of reactivities of the two compounds. The k_1 were found to be fairly proportional to the amount of catalyst. Average values

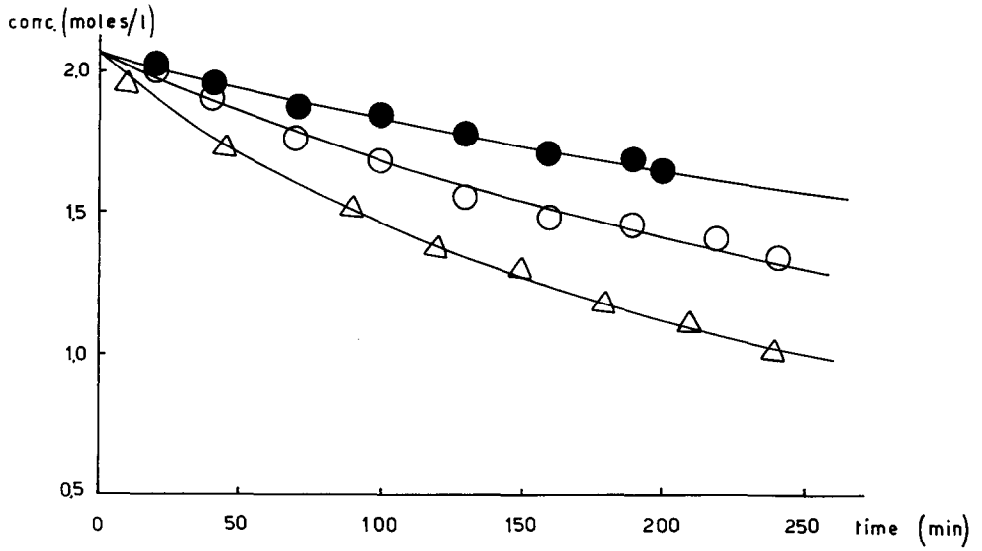


FIG. 2. Reactions of cyclohexene at 50.3°C on variable amounts of catalyst: ●, 100 mg; ○, 200 mg; △, 400 mg. Solid lines calculated from Eq. (5).

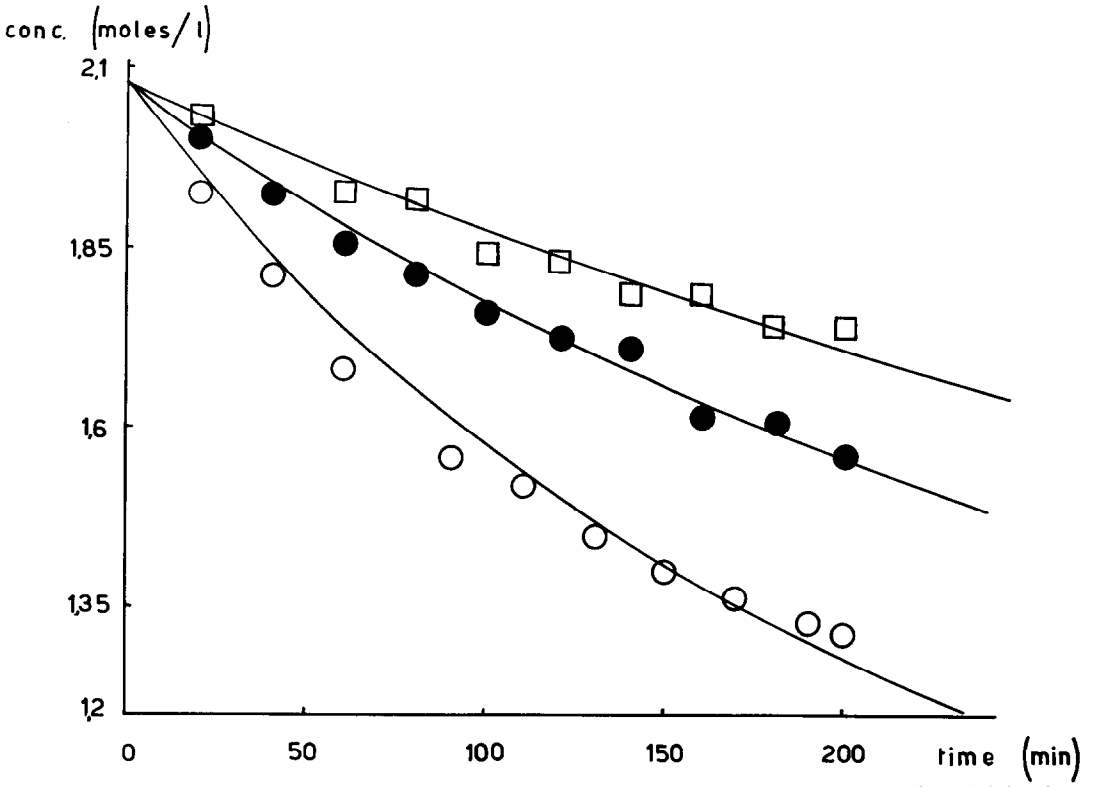


FIG. 3. Reactions of cyclohexene at 60.5°C on 200 mg Pd with benzene present in the initial solutions: ○, no benzene; ●, 5 ml C_6H_6; □, 10 ml C_6H_6. Solid lines calculated from Eq. (5).

of the constants, referred to 100 mg of palladium, are given in Table 1.

TABLE 1
APPROXIMATE EVALUATION OF REACTIVITIES IN RUNS STARTING FROM CYCLOHEXADIENE

Temperature (°C)	$10^2 \times (k_1)_A$ for cyclohexadiene (min^{-1}/100 mg Pd)	$10^2 \times (k_1)_B$ for cyclohexene (min^{-1}/100 mg Pd)
50.3	2.4	0.13
55.3	3.4	0.10
60.5	5.2	0.13

Kinetics of Cyclohexene Disproportionation

In a more accurate treatment of the kinetics, the rate-determining step of the cyclohexene reaction was assumed to be bimolecular with respect to the reagent on the catalyst (see Discussion). The following rate law corresponds to this hypothesis, taking into account the adsorption on the catalyst surface of reagent and products:

$$r = -dc_B/dt = kb_B^2c_B^2/(1 + \sum_j b_jc_j)^2 \quad (2)$$

where c_j and b_j are, respectively, the molar concentration and the adsorption constant of the jth component (B = cyclohexene) and k is the rate constant.

The concentration of cyclohexadiene analytically determined is very small (much lower than that of benzene), and its adsorption constant is likely to be of the same order of magnitude as the benzene one. Moreover it seems reasonable that cyclohexane (as of course THF) is only weakly adsorbed. On this basis we approximated Eq. (2) to

$$r = -dc_B/dt = kb_B^2c_B^2/(1 + b_Bc_B + b_Xc_X)^2 \quad (3)$$

where X stands for benzene.

From Eq. (1) and neglecting the cyclohexadiene instantaneous concentration, it comes out

$$c_X = c_X^\circ + \tfrac{1}{3}(c_B^\circ - c_B) \quad (4)$$

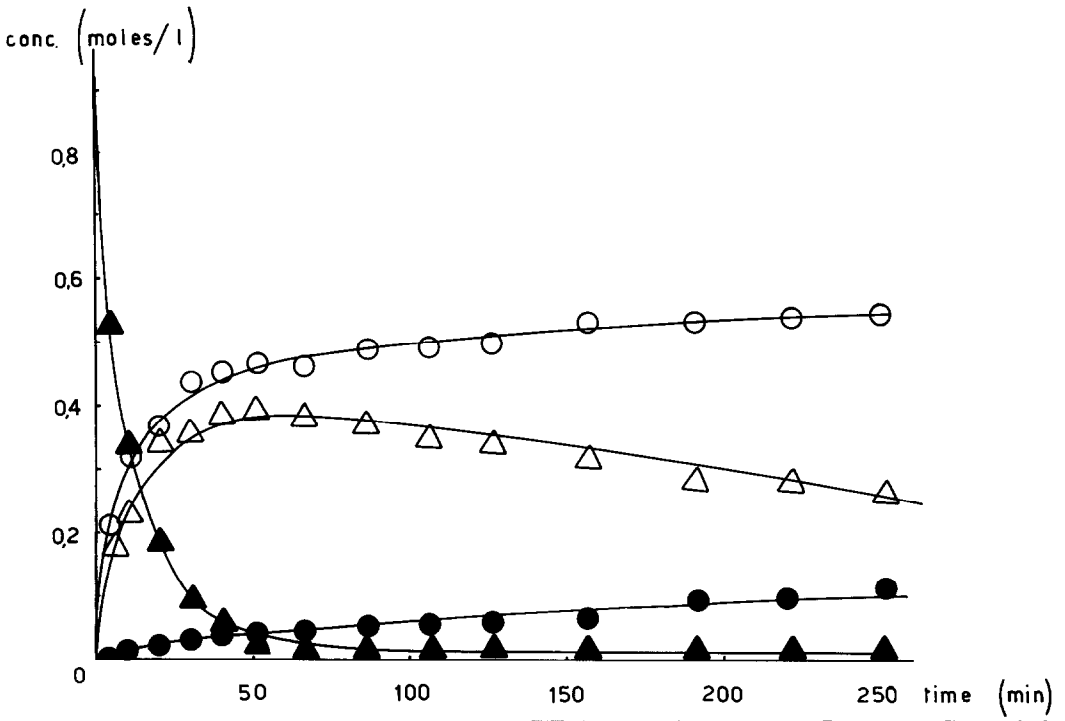


FIG. 4. Reaction of 0.920 M cyclohexadiene in THF (ca. 55 ml) on 200 mg Pd at 55.3°C; symbols as in Fig. 1. Solid lines drawn to smooth the experimental points.

Substituting into (3) and integrating one obtains:

$$t = (kb_B^2)^{-1}\{[1 + b_X(\tfrac{1}{3}c_B^\circ + c_X^\circ)]^2 \cdot (c_B^{-1} - c_B^{\circ -1}) + 2[1 + b_X(\tfrac{1}{3}c_B^\circ + c_X^\circ)] \cdot (b_B - \tfrac{1}{3}b_X) \ln (c_B^\circ/c_B) + (b_B - \tfrac{1}{3}b_X)^2(c_B^\circ - c_B)\} \quad (5)$$

The parameters k, b_B, and b_X could have been determined by evaluating (dc_B/dt) at different times, and using Eq. (3). However the evaluation of such derivatives (graphically or numerically) from kinetic experimental data is affected by large errors. For this reason we preferred to apply Eq. (5), looking for the values of the parameters by fitting of the equation to the experimental c_B, t data.

A systematic procedure to do so is to start from arbitrary values k, b_B, and b_X, to calculate with them a set of time values (t_c) corresponding to the experimental c_B's and seek the minimum of the function

$$F(k,b_B,b_X) = \Sigma_i[t_c(k,b_B,b_X) - t]^2 \quad (6)$$

where the sum is extended over all the experimental points of the run under consideration and t's are the observed values of the time. As the function $F(k,b_B,b_X)$ is nonlinear in the variables it cannot be minimized directly and so we chose a numerical procedure based on the steepest-descent method. Details of the calculation are reported in Appendix.

The results for different runs at the same temperature were averaged (referring to 100 mg Pd) and the values reported in Table 2 were obtained. Results of the additional runs with added benzene are shown in Table 3.

Linear plots of log b_B, log b_X, and log k vs $(1/T)$ are reported in Fig. 5. From the slopes of the lines the standard heats of adsorption of cyclohexene and benzene were evaluated through Eq. (7)

$$b = \exp[-(\Delta H^\circ_a/RT) + (\Delta S^\circ_a/R)] \quad (7)$$

and the energy of activation of the reaction through the Arrhenius equation. Standard entropies of adsorption and the entropy of

TABLE 2
KINETIC DATA FOR CYCLOHEXENE REACTIONS (EQ. 5)

Temperature (°C)	b_B (liter/mole)	b_X (liter/mole)	k (moles/liter min 100 mg Pd)
50.3	0.233 ± 0.002	1.25 ± 0.00	0.0236 ± 0.0007
55.3	0.194 ± 0.006	1.00 ± 0.00	0.031 ± 0.002
60.5	0.181 ± 0.002	0.801 ± 0.000	0.073 ± 0.011

TABLE 3
ADDITIONAL RUNS WITH ADDED BENZENE[a]

Initial benzene conc.	b_B (liter/mole)	b_X (liter/mole)	k (moles/liter min 100 mg Pd)
$c°_X = 0$	0.178	0.802	0.047
$c°_X = 0.445\ M$	0.177	0.802	0.039
$c°_X = 0.890\ M$	0.178	0.802	0.036

[a] At 60.5°C with the less active catalyst.

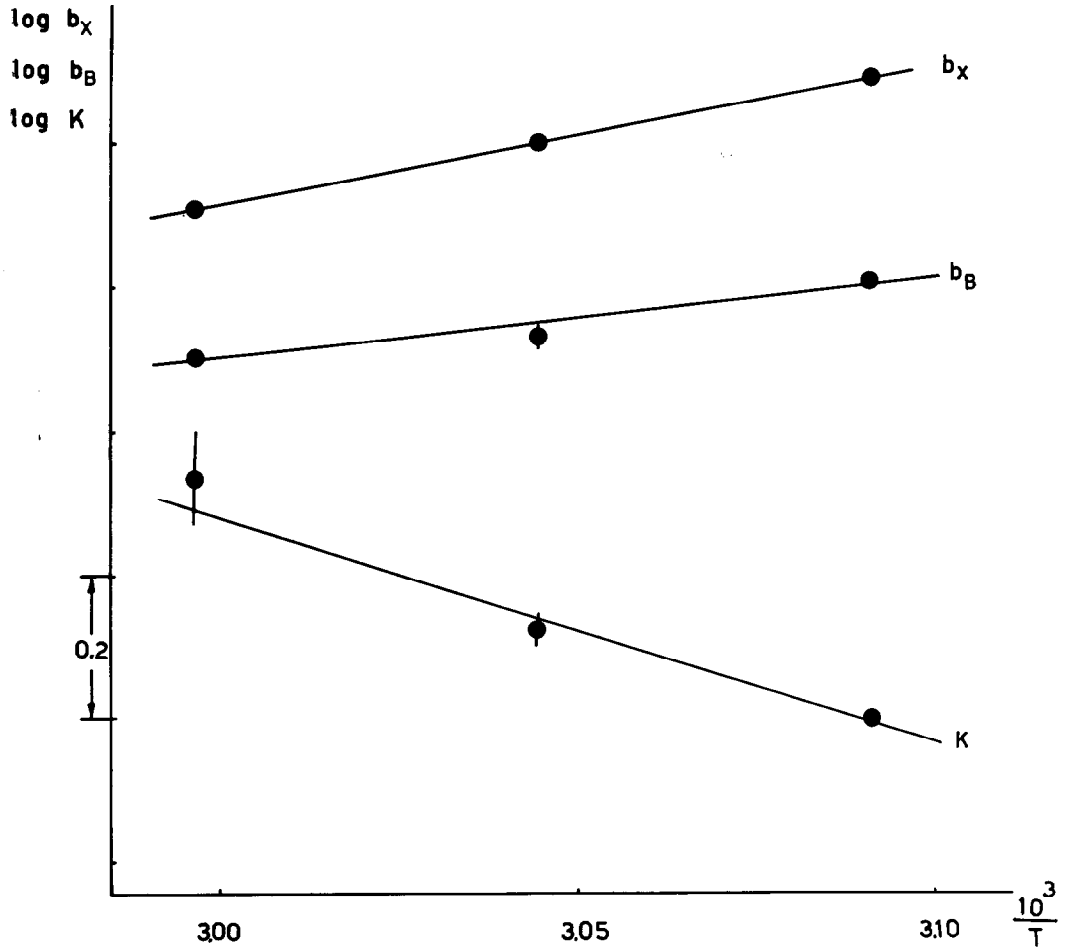


FIG. 5. Log b_X, log b_B, and log k vs $(1/T)$. Each plot has a different zero for the ordinate.

activation were also calculated from Eq. (7) and Eq. (8) (6*a*)

$$k = (KT/h) \exp [-(\Delta H‡/RT) + (\Delta S‡/R)] \quad (8)$$

The results are the following

Cyclohexene	$-\Delta H°_a = 5.2$ kcal/mole
	$\Delta S°_a = -19$ cal/mole °K
Benzene	$-\Delta H°_a = 9.3$ kcal/mole
	$\Delta S°_a = -28$ cal/mole °K
	$\Delta E‡ = 14$ kcal/mole
	$\Delta S‡ = -19$ cal/mole °K

The uncertainty in the activation energy has been estimated as ±2 kcal/mole.

Because of our definition of the b_j constants, the standard enthalpies and entropies of adsorption are referred to 1 M solutions in the THF.

A theoretical calculation of benzene standard adsorption entropy has been performed according to Trapnell (*7*). The translational and rotational contributions to the entropy of a gas are given by well-known formulas (*6b*)

$$S°_g = S°_{t3} + S°_r = (\tfrac{3}{2}R \ln M + \tfrac{5}{2}R \ln T - R \ln p - 2.2)8) + (\tfrac{3}{2}R \ln T + \tfrac{1}{2}R \ln (I_x I_y I_z) - R \ln \sigma + 267.54) \quad (9)$$

where I_x, I_y, I_z are moments of inertia about axes x, y, z, and σ (symmetry number) is equal to 12 for benzene. Vibrational and electronic contributions are omitted assuming that they are not changed by chemisorption. $S°_g$ has been calculated by Eq. (9) for the gas in equilibrium at 50°C with a 1 M benzene solution in THF ($p = 0.0291$ atm). For the adsorbed benzene two limiting cases were considered, one with complete loss of translational and rotational entropy ("immobile" molecule), the other with loss of only one translational degree of freedom and retention of all rotational and residual translational entropy ("mobile" molecule). In the "immobile" case a configurational contribution to the entropy has to be taken into account

$$S_c = -R\{\ln \theta + [(1 - \theta)/\theta] \ln (1 - \theta)\} \quad (10)$$

where θ = coverage. Therefore the calculated adsorption entropy comes out as

$$\Delta S°_{im} = S°_c - S°_g \quad (11)$$

Taking $\theta = 0.5$ we obtained $\Delta S°_{im} = 2.75 - (46.43 + 20.76) = -64.44$ e.u.

In the "mobile" case, the sum of the translational and rotational entropies is given by

$$S°_a = S°_{t2} + S°_r$$

where $S°_r$ has the same meaning as in Eq. (9), and it is

$$S°_{t2} = R \ln MTA + 65.80$$

A being the area occupied by the benzene molecule. The result of the calculation (with $A = 35.4$ Å^2) was

$$\Delta S°_m = S°_a - S°_g = S°_{t2} - S°_{t3} = 19.81 - 46.43 = -26.62 \text{ e.u.}$$

A precise calculation has not been made for cyclohexene but the close similarity of geometrical and physical properties of cyclohexene and benzene suggests that analogous values would be obtained for $\Delta S°_{im}$ and $\Delta S°_m$.

In order to compare the experimental values of $\Delta S°_a$ given above with the calculated values, the first ones should be increased by three terms, one corresponding to compression of gaseous benzene from 0.0291 atm to its vapor pressure at 50°, the second to the condensation entropy, and the third to the solution entropy. Neglecting the last term, there are obtained:

for cyclohexene $\Delta S°_{ag} = -48$ e.u.
for benzene $\Delta S°_{ag} = -57$ e.u.

Discussion

It has been confirmed that the reaction of cyclohexene on palladium at low temperature is a self-hydrogenation. The intervention of a dehydrogenation reaction would give R values sensibly lower than unity and dependent on the temperature, as found for instance by C. Kemball *et al.* on gold (*8*). Our values are so close to unity that no meaning can be validly attached to the small deviation. This is evidence that the reagents' adsorption is not dissociative.

In order to compare the reactivities of cyclohexadiene and cyclohexene, pseudo-first order rate constants for the latter were determined following, for consistency, the reaction of the cyclohexene produced from

cyclohexadiene. The values are reported in Table 1.

The diene is more reactive than cyclohexene by an average factor of 31. These findings are in remarkable contrast with the factor 2 reported by Linstead *et al.* (*3a*). However these authors gave first order constants for cyclohexene at about 65° (*3b*) that are an order of magnitude larger than our values, making the comparison at the same catalyst concentration. This proves that our catalyst was less active. (The second batch gave a palladium black even less active.)

An obvious consequence of the large reactivity ratio now found is that cyclohexadiene cannot be easily ruled out as an intermediate of cyclohexene disproportionation, even if its high decomposition rate makes its concentration during the course of the reaction very low and difficult to evaluate. Roughly interpreting the cyclohexene disproportionation as due to two consecutive first order reactions [cyclohexene (B) → cyclohexadiene (A) → products] and using the pseudostationary state approximation (*9*) one obtains

$$[A]_{ps} = \{(k_1)_B/(k_1)_A\}[B]$$

so that cyclohexadiene would be at any time about 3.2% of cyclohexene. In the runs where cyclohexadiene has been better evaluated it has been found as 2.8% of cyclohexene on the average. In other cases its concentration was less, but of the order of 1% with respect to cyclohexene.

On this basis we argued that the process could be controlled by a second order rate-determining reaction between two cyclohexene molecules adsorbed on the catalyst.

The set of runs with added benzene (X) proved the influence of this product on the reaction kinetics, as shown in Fig. 3. (The pseudo-first order constants are $10^2 \times k_1$ ($\text{min}^{-1}/100$ mg Pd) = 0.14 at $c^\circ_X = 0$; 0.078 at $c^\circ_X = 0.445$ M; 0.056 at $c^\circ_X = 0.890$ M.) These considerations led to the use of Eqs. (3) and (5), that actually proved to fit well the experimental results (Figs. 1, 2, 3).

The examination of the average adsorption coefficients thus found (Table 2) shows that benzene is more strongly chemisorbed than cyclohexene ($b_X/b_B \simeq 5$). The difference in unsaturation can account for this. Experimental adsorption entropies (ΔS°_{ag}) of the two molecular species have values lying between the theoretically evaluated ΔS°_{im} and ΔS°_m, but closer to the former. This analysis shows that particularly benzene molecules are almost immobile when chemisorbed. Adsorption heats, referred to the gas phase (ΔH_{ev} = 7.7 kcal/mole for both compounds) are: $-\Delta H^\circ_{ag}$ = 12.9 kcal/mole for cyclohexene; 17 kcal/mole for benzene. The latter value compares well with the adsorption heat of benzene on nickel, reported as ca. 30 kcal/mole at zero coverage and ca. 7 kcal/mole at high coverage (*10*).

On the basis of all experimental results we suggest that the rate-determining step of cyclohexene disproportionation on palladium is a direct hydrogen transfer between two adsorbed molecules, according to a donor–acceptor mechanism. One molecule, associatively chemisorbed by means of its π electrons, acts as acceptor of one or two hydrogen atoms donated by methylenic groups of another similarly chemisorbed molecule. A single step of the process may be described by the scheme shown on the next page, where the star stands for a site on the catalyst and dashed lines indicate partial bonds. A succession of steps of this kind can give rise to cyclohexane and a series of chemisorbed species, among which cyclohexene, cyclohexadiene, and benzene would be in equilibrium with the liquid phase.

In order to better ascertain the advanced stages of the reaction further work on cyclohexadiene is now in progress. The competition of cyclohexene and cyclohexadiene as acceptors of hydrogen from a cyclohexadiene donor is one of the interesting problems to be solved.

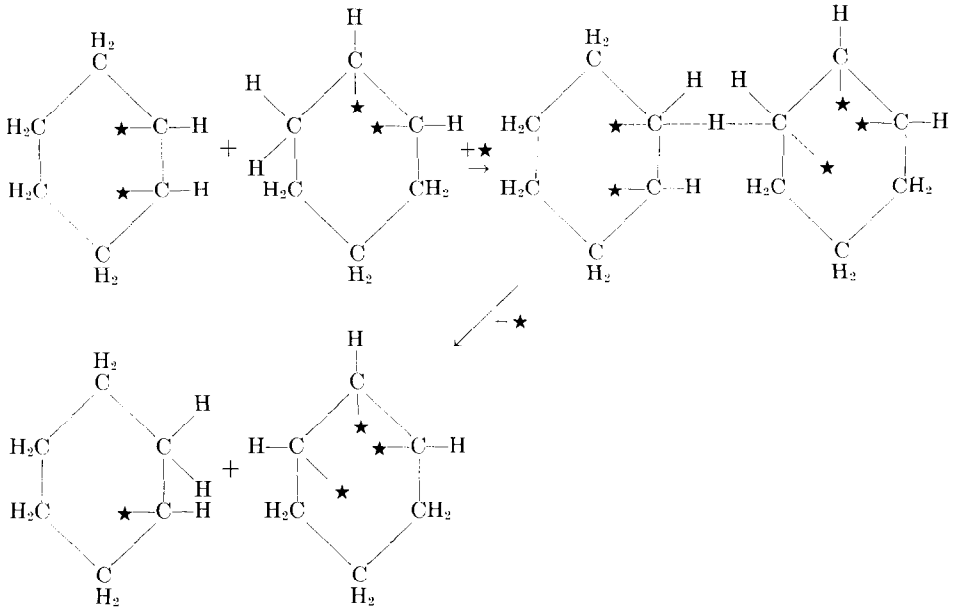
ACKNOWLEDGMENT

We thank Dr. (Miss) C. Mariani for valuable help in computational work.

APPENDIX

The vector

$$\mathbf{G} = \text{grad } F = (\partial F/\partial k)\mathbf{i} + (\partial F/\partial b_B)\mathbf{j} + (\partial F/\partial b_X)\mathbf{k}$$



gives the direction of steepest variation of the function F (Eq. 6).

The search of the minimum has been done by a stepwise procedure through successive increments of the variables k, b_B, b_X taken proportional to the corresponding components of **G**, e.g.

$$\delta b_B = \lambda(\partial F/\partial b_B)$$

For a more rapid convergence we evaluated in every step a value of λ which gave increments δk, δb_B, δb_X such as to minimize $|\mathbf{G}|$. Applying the Newton procedure to the derivative function of $|\mathbf{G}|$ and employing the usual finite difference method, λ is given by

$$\lambda = \frac{\Delta\lambda}{2} \cdot \frac{|\mathbf{G}_-| - |\mathbf{G}_+|}{|\mathbf{G}_+| + |\mathbf{G}_-| - 2|\mathbf{G}_0|}$$

where

$|\mathbf{G}_0|$ = modulus of **G** evaluated at point (k, b_B, b_X);

$|\mathbf{G}_+|$ = modulus of **G** evaluated at point

$[k + \Delta\lambda(\partial F/\partial k),\ b_B + \Delta\lambda(\partial F/\partial b_B),\ b_X + \Delta\lambda(\partial F/\partial b_X)]$;

$|\mathbf{G}_-|$ = modulus of **G** evaluated at point

$[k - \Delta\lambda(\partial F/\partial k),\ b_B - \Delta\lambda(\partial F/\partial b_B),\ b_X - \Delta\lambda(\partial F/\partial b_X)]$.

Also, the derivatives of F were calculated through a finite difference procedure. The increments used for derivation were the following: $\Delta\lambda = 10^{-7}$; $\Delta k = 10^{-5}$; $\Delta b_B = \Delta b_X = 10^{-4}$. The iterative computation was carried on until the components of **G** were small enough. All the calculations were performed with a Remington Rand model USS computer.

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