(no symmetry). In any of these structures, all vibrations would be both infrared- and Raman-active except for the infrared-silent vibrations of species A_2 of C_{2v}. Therefore the vibrational selection rules are unfavorable *a priori* for a structural decision, and in addition the failure of numerous vibrations to appear in the Raman effect renders firm decision impossible.

The most significant structural evidence is furnished by the type-C infrared bands. The number of these found is just that predicted for C_{2v} symmetry for both cyclobutene and cyclobutene-d_6. The frequencies and band shapes (see Fig. 3) are those expected and the frequency product ratio for species B_2 agrees with the theoretical value. To be sure, these things might happen by accident for a structure of lesser symmetry, particularly if the deviation from C_{2v} geometry were rather small. The best one can say is that there is some rather definite evidence in favor of a C_{2v} structure and nothing compelling against it. High-resolution study of the rotation-vibration spectra for bands of all three types in both molecules should furnish sufficient information to evaluate the most important geometrical parameters.

An interesting result of this study is the unusual location and intensity of the double bond frequency. Presumably the low frequency is the result of a decrease in the C=C force constant due to strain in the four-membered ring,[17] as was pointed out above. The high intensity of the double bond vibration in the Raman effect is remarkable, as is the unusually low intensity of the infrared band. The latter, which is weaker than the overtone bands at 1540 and 1760, cannot be used with assurance to indicate the presence of HC=CH in a four-membered ring, and particularly its absence from an infrared spectrum is not an indication of the absence of this group from a molecule. The Raman spectrum is a more reliable guide for this purpose.[18] Substitution of one of the hydrogens by methyl, halogen, or other group will of course affect both the frequency and intensity of the C=C infrared absorption band.

Thermodynamic Functions of Cyclobutene

So far as the authors are aware, no investigation has been made of the heat capacity and heats of transition of cyclobutene. It is therefore not possible to check the assignment given in Table IV by comparison of calculated with measured entropy, free energy or heat capacity. Calculation of these quantities has been carried out by Mr. Alfred Danti of this Laboratory and these results will be published separately.

CAMBRIDGE, MASS.

[17] J. O. Halford (*J. Chem. Phys.*, **24**, 830 (1956)) has shown that a considerable variation in the carbonyl frequency of ketones could result without changing the force constants simply by a change of the bond angles of the carbonyl group. Possibly a similar effect is partially responsible for the low C=C frequency in cyclobutene.

[18] D. E. Applequist and J. D. Roberts (THIS JOURNAL, **78**, 4012 (1956)) have recently published infrared spectra of methylenecyclobutene and certain related compounds. Although the exocyclic double bond of methylenecyclobutene gives a strong infrared absorption band at about 1670 cm.$^{-1}$, no band is reported near 1550 cm.$^{-1}$ for the internal double bond. In the Raman spectrum of this compound, on the other hand (M. V. Evans and R. C. Lord, unpublished results), both double bond frequencies are present, at 1673 and 1530 cm.$^{-1}$, respectively, the latter being considerably stronger.

[CONTRIBUTION FROM THE CRYOGENIC LABORATORY AND DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Surface Catalysis of the Ortho- to Para- Conversion in Hydrogen under Pressure at Low Temperatures

BY DOUGLAS S. CHAPIN[1] AND HERRICK L. JOHNSTON

RECEIVED OCTOBER 5, 1956

The surface catalysis of the ortho- to para- conversion in hydrogen was investigated on a series of catalysts consisting of 0.05 to 2.47% chromia–alumina under pressures in the range 5 to 100 atmospheres at 77°K. and on a 0.05% chromia–alumina catalyst at approximately 29 atm. in the region 55–195°K. For catalysts of lower chromia concentrations the half-life varied linearly with pressure and linearly with the reciprocal of the number of gram-atoms of chromium in the catalyst chamber. The rate data, which were first order with respect to composition, support the theory of Harrison and McDowell[2] who adapted the Wigner[3] theory to the case of conversion in a physically adsorbed hydrogen layer on a paramagnetic surface. The rate constant temperature dependency, in agreement with this theory, was positive for the case of high hydrogen surface coverage investigated in this research. This is in contrast to the negative temperature dependency of the rate constant usually observed for the case of low surface coverage. Absolute rate calculations were made for the case of high surface coverage using Harrison and McDowell's choice of reasonable values for certain constants in the rate expression. Good agreement with experiment was obtained.

Introduction

Though considerable experimental work has been done concerning the surface catalysis of the ortho–para- conversion in hydrogen at pressures of 1 atm. or less, the catalysis at higher pressures and low temperatures has been little studied since the initial experiments of Bonhoeffer and Harteck[4] and Farkas and Bonhoeffer[5] to prove the existence of the heterogeneous catalysis.

Harrison and McDowell,[2] in their study of the para–orthohydrogen conversion on the free radical α,α-diphenyl-β-picrylhydrazyl at low temperatures and pressures, concluded that the conversion takes place by interaction between hydrogen mole-

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[2] L. G. Harrison and C. A. McDowell, *Proc. Roy. Soc.* (*London*), **A220**, 77 (1953).

[3] E. Wigner, *Z. physik. Chem.*, **B23**, 28 (1933).

[4] K. F. Bonhoeffer and P. Harteck, *ibid.*, **B4**, 113 (1929).

[5] A. Farkas and K. F. Bonhoeffer, *ibid.*, Bodensteinband, 638 (1931).

cules in a mobile physically adsorbed layer and paramagnetic sites. By using the transition probabilities given by Wigner[3] and by calculating the fraction of the time a molecule spends over a paramagnetic site while moving as a two-dimensional gas in the adsorbed layer, Harrison and McDowell developed an absolute rate expression. This expression predicts in agreement with experiment a negative temperature dependency of the rate constant and independence of the rate constant with pressure. Absolute rate calculations for the case of low surface coverage were in agreement with experiment when reasonable values were used for the various constants involved.

The present work is concerned with an experimental study of the variation of the rate constant with temperature, pressure and number of paramagnetic sites for the case of high surface coverages. The rate investigations were carried out by the static method on impregnation catalysts of several concentrations of Cr_2O_3–Al_2O_3 with most of the work being done on 0.05 and 0.24% chromia–alumina.

Theoretical Development

The conversion follows the usual unimolecular rate law

$$u_t = u_0 e^{-k_H t} \qquad (1)$$

where $u_t = x_t - x_e$ and $u_0 = x_0 - x_e$ in which x_t, x_0 and x_e are the percentages of parahydrogen at time $t = t$, 0 and ∞, respectively; and k_H is the rate constant. In order to compare theoretical and experimental results the rate constant and the variables upon which it theoretically depends are given below; but no reproduction of the considerations leading to this rate expression is given here. The general expression Harrison and McDowell obtained for the rate constant for a parahydrogen conversion taking place in a physically adsorbed layer is given by

$$k_H = \frac{sK\rho a\,(RTM)^{1/2}\overline{l^2}G(T)}{\sqrt{2}r_s^8 Np v\beta_0 l_m}\left(\frac{\alpha_0\mu e^{Q/RT}}{1 + \frac{\alpha_0\mu}{\beta_0\nu}e^{Q/RT}}\right) \qquad (2)$$

where s is the total surface area in sq. cm.; ρ is the number of active sites per sq. cm.; a is the area per paramagnetic site in sq. cm.; ν is the number of hydrogen molecules per sq. cm. in a complete monolayer; r_s is the mean distance of a hydrogen molecule from the surface in a physically adsorbed layer; p is the pressure; v is the volume of the system; T is the absolute temperature; M is the molecular weight of hydrogen; R is the gas constant; N is Avogadro's number; $\overline{l^2}/l_m$ is the ratio of the mean square path to the mean path across an idealized circle of interaction for a molecule of hydrogen moving in the adsorbed layer. Also in equation 2, α_0 is the condensation coefficient, which is independent of temperature assuming no activation energy of adsorption; β_0 is a desorption coefficient, which is independent of temperature and $\mu = pN/(2\pi MRT)^{1/2}$ is the rate molecules of hydrogen strike one sq. cm. of surface per sec.; Q is the activation energy of desorption. Again, in equation 2, K is given by

$$K = \frac{24\mu_a^2\mu_p^2 I\pi^2}{h^2 m} \qquad (3)$$

where μ_a is the magnetic moment of each paramagnetic surface site; μ_p is the proton magnetic moment; I is the moment of inertia of a hydrogen molecule of mass m; and h is Planck's constant. $G(T)$ in equation 2 is given by

$$G(T) = \left\{1 + \frac{n_p(T)}{n_0(T)}\right\}\left\{\frac{\sum\limits_{J = 0,1,2,\ldots} J\exp(-E_J/kT)}{\sum\limits_{J = 0,2,4,\ldots}(2J + 1)\exp(-E_J/kT)}\right\} \qquad (4)$$

where $n_p(T)$ and $n_0(T)$ are the equilibrium concentrations of para- and orthohydrogen, respectively, at the temperature T; J is the rotational quantum number and E_J is the rotational energy of the molecule in the state J given by

$$E_J = J(J + 1)h^2/(8\pi^2 I) \qquad (5)$$

Substitution of $\mu = pN/(2\pi MRT)^{1/2}$ in equation 2 yields

$$k_H = \frac{ACT^{1/2}G(T)}{T^{1/2}e^{-Q/RT} + Bp} \qquad (6)$$

where

$$A = \frac{NKa\alpha_0\overline{l^2}}{2\pi^{1/2}v\beta_0 r_s^8 l_m} \text{ and } B = \frac{\alpha_0 N}{\beta_0\nu(2\pi MR)^{1/2}}$$

The total number of moles, C, of paramagnetic sites exposed on the surface to hydrogen conversion is given by $C = s\rho/N$.

Noting that the half-life $\tau_{1/2} = \ln 2/k_H$ and utilizing equation 6, the half-life time is given by

$$\tau_{1/2} = \frac{\ln 2}{AG(T)C}\left(\frac{Bp}{T^{1/2}} + e^{-Q/RT}\right) \qquad (7)$$

As approximations, at sufficiently low pressures the first term in equation 7 can be neglected; at sufficiently high pressures the second term can be neglected. Thus for high pressures approximately

$$\tau_{1/2} = \frac{Bp\ln 2}{AT^{1/2}G(T)C} \qquad (8)$$

These equations (particularly equation 7) will be examined subsequently in the light of the experimental determination of the pressure, concentration and temperature dependencies of the heterogeneous ortho–parahydrogen conversion at low temperatures under pressure in contact with chromia–alumina catalysts.

Experimental

Rate Apparatus.—The apparatus for the rate determinations consisted essentially of a stainless steel cylinder 1 in. i.d. of 200-cc. volume, suspended from a brass cover plate which closed the end of a standard brass cryostat typical of those used in this Laboratory. Unsilvered slit windows in the glass dewar were visible through opposing Lucite windows in the cryostat. In a run specially purified hydrogen under pressure could be expanded from a 1.5-l. calibrated cylinder on to the catalyst previously conditioned in the catalyst chamber. Liquid nitrogen was the cryostating bath in the majority of the runs. Samples of hydrogen were withdrawn through a 0.009 in. i.d. stainless steel capillary tube extending into the mid-region of the chamber. A capillary lock between two specially designed valves allowed eight locks of purge preceding each of twelve samples to be taken with a total hydrogen depletion of less than 0.1% of the total amount of hydrogen in the chamber. Pressures before and after expansion of the hydrogen were read by means of a Bourdon laboratory test gage which had been calibrated with a dead weight gage.

Analytical Apparatus.—Samples stored in a series of Pyrex bulbs over mercury were analyzed using the Farkas microthermal conductivity method, employing a pressure of 0.05 mm.[6,7] The cell was calibrated with mixtures prepared volumetrically from normal and 50% parahydrogen. The calibration curve showed a maximum deviation of 2% at a concentration corresponding to $u_t/u_0 = 0.5$. The precision of the cell was approximately 0.2% in u_t/u_0 at 0.5.

Surface Area Apparatus.—Surface areas were measured volumetrically at liquid nitrogen temperature using the BET[8] method in which the volume of nitrogen required to form a monolayer on the catalyst surface was estimated from the adsorption isotherms.

Hydrogen Purification.—Hydrogen obtained from the hydrogen liquefaction cycle of this Laboratory was initially purified by passage through a liquid nitrogen trap, over platinized asbestos at 400° and through another liquid nitrogen trap. This procedure removed the condensable impurities, converted oxygen to water and removed the water formed, respectively. The platinized asbestos also served to equilibrate the hydrogen to normal with respect to its ortho-parahydrogen composition. Final purification was effected by liquefaction, filtration through glass wool to remove any solid nitrogen present, gasification, second liquefaction and distillation. High pressure pure hydrogen was obtained by condensing this hydrogen into a heavy copper chamber immersed in liquid hydrogen with subsequent isolation and then by heating the copper chamber while it was connected to a storage cylinder at room temperature.

Catalyst Preparation.—Special Bayer-process alumina in the form of $^1/_8$ in. pellets of low iron content was prepared in a 50 lb. lot by the Harshaw Chemical Company. The composition was stated by the manufacturer to be as follows: SiO_2, 0.03%; Fe_2O_3, 0.008%; TiO_2, 0.007%; Na_2O, 0.4%; and Al_2O_3, 99.+%. This carrier was heated to 600° for 16 hours, appeared snow white, and will be called the unleached carrier. Leached carrier was prepared by agitating 450 g. of the unleached carrier with 500 ml. of 1 *N* HNO_3 for 16 hours. This was followed by washing overnight with 7.5 gallons of double distilled water, drying and calcining at 600° for 16 hours. The surface area decreased from 94.9 to 87.4 sq. m./g. The loss in weight due only to acid action was not determined. Catalysts of various chromia concentrations in the range 0–2% were prepared by agitating 228.3 g. of the carrier with 200 ml. of chromic acid solution of the appropriate concentration. Reagent grade CrO_3 from Baker and Adamson Chemical Company was used. The stated maximum impurity of Fe, Al, Ba, etc., was 0.03%. The carrier and chromic acid were sealed in a liter glass-stoppered bottle and rolled slowly for 16 hours, then washed with 4 l. of double distilled water. The bright yellow pellets were dried at 110° for several hours and heated for 16 hours at 300°. The product at this point was bright with small dark patches which were thought due to partial reduction. Reduction to a uniform green chromic oxide was accomplished by passing hydrogen over the catalyst at 350° for 5 hours.

Chromium Analysis.—Solutions of chromic acid were analyzed by adding a known excess of ferrous ammonium sulfate and back titrating with standard potassium dichromate in a 1.5 *M* phosphoric–5 *M* sulfuric acid media with diphenylamine sulfonate indicator.[9] Chromia–alumina catalysts were analyzed by the same method after fusion with sodium peroxide followed by careful neutralization with 6 *N* sulfuric acid.

Pretreatment of Catalysts.—The usual pretreatment procedure was to pump at room temperature for 24 hours on approximately 175 g. of catalyst sealed in the high pressure chamber. This was followed by pumping 24 hours at 200°. Hydrogen from the purification train previously mentioned was passed slowly over the catalyst at 200° for 3 hours. Then the catalyst was pumped while cooling down to "run" temperature. At this temperature the catalyst was purged several times with some of the specially prepared high pressure hydrogen. The chamber was pumped after this treatment until the start of a catalytic run, which usually took place within a few hours after the final purge. The only treatment between runs on the same catalyst was to evacuate the chamber at low temperatures.

Catalytic Runs.—Specially purified hydrogen was expanded onto the evacuated catalyst from a calibrated cylinder. The drop in pressure and the cylinder temperature were used to calculate the amount of gas delivered to the catalyst chamber. Temperature was measured with a copper–constantan thermocouple.

Results

Catalysts.—Nitrogen surface areas on the catalysts prepared from the leached carrier were very nearly independent of chromia concentration. Surface areas for 0.00, 0.0486 and 1.08% chromia–alumina catalysts were 87.4, 87.6 and 86.7 sq. m./g., respectively. Adsorption isotherms for the up-take of chromic acid on the leached and unleached alumina carrier during the preparation of the chromia–alumina catalysts showed an increase of amount of chromic acid adsorbed with increasing final chromic acid concentration. Adsorption on the leached carrier was approximately five to ten times that on the unleached carrier for a given final concentration of chromic acid at lower (less than 0.05 mole/l.) concentrations. The isotherm for the unleached carrier leveled off at a chromic acid adsorption corresponding to a catalyst composition of 1.78% chromia–alumina by weight. It is assumed that essentially all chromic acid molecules or ions that are adsorbed on the alumina will do so in pores which are large enough for hydrogen to penetrate in the dried catalyst so that analysis of the finished catalyst for chromium is an effective measure of the number of paramagnetic sites available for reaction. Cunningham and Johnston[10] found that the rate constant in the heterogeneous liquid hydrogen conversion on several of the same catalysts used in this work varied linearly with the chromia concentration. This would seem to indicate that the chromic acid is adsorbed on the alumina in essentially a monolayer.

Rate Data.—Rate constants for the ortho-parahydrogen conversion on chromia–alumina catalysts were obtained from the slope of the line produced by plotting ln (u_0/u_t) *vs.* t (equation 1). Figs. 1, 2 and 3 show these plots for 0.0486 and 0.237% chromia–alumina under several conditions of temperature and pressure. In these plots time has been adjusted so as to give coincidence with the origin.

A summary of the rate data is given in Tables I and II. The first column gives the run designation. The 2S series runs were made on the unimpregnated leached alumina carrier which was used in the majority of the runs. The carrier and catalysts were in the form of $^1/_8$ in. pellets. The 2S series blank runs were used to correct the low concentration runs for the catalytic activity of the carrier. Conditions of temperature and pressure for the runs within a series were changed in the order given by the second number in the first column. The total number of g.-atom of chromium in the catalyst chamber and assumed to be available for interaction with the hydrogen is given in the second

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[6] A. Farkas, *Z. physik. Chem.*, **B22**, 344 (1933).

[7] A. Farkas, "Orthohydrogen, Parahydrogen and Heavy Hydrogen," Cambridge University Press, 1935, p. 25.

[8] S. Brunauer, P. H. Emmett and E. Teller, THIS JOURNAL, **60**, 309 (1938).

[9] A. R. Olson, E. F. Orlemann and C. W. Koch, "Introductory Quantitative Analysis," W. H. Freeman and Company, San Francisco, Cal., 1948, p. 228.

[10] C. M. Cunningham and H. L. Johnston, to be published.

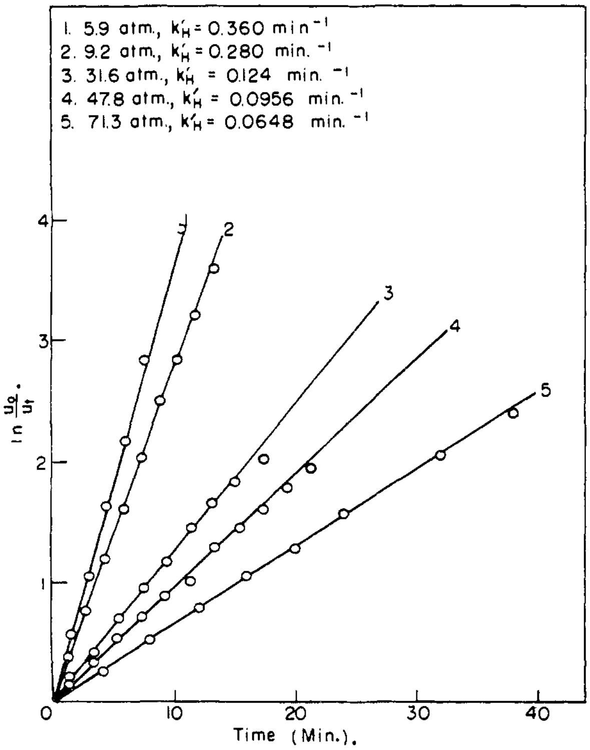

Fig. 1.—Ortho-para hydrogen conversion on 0.0486% Cr_2O_3–Al_2O_3 at 77°K. and various pressures.

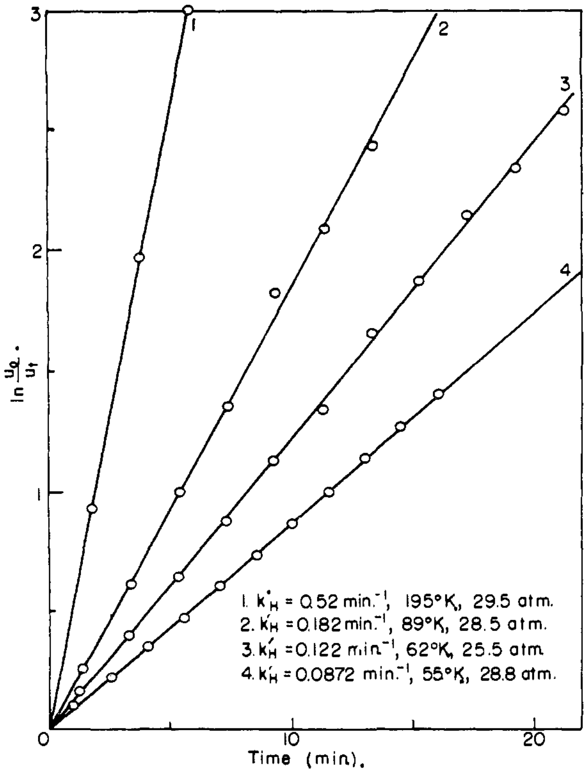

Fig. 2.—Ortho-para hydrogen conversion on 0.0486% Cr_2O_3–Al_2O_3 at various temperatures and approximately 28 atm.

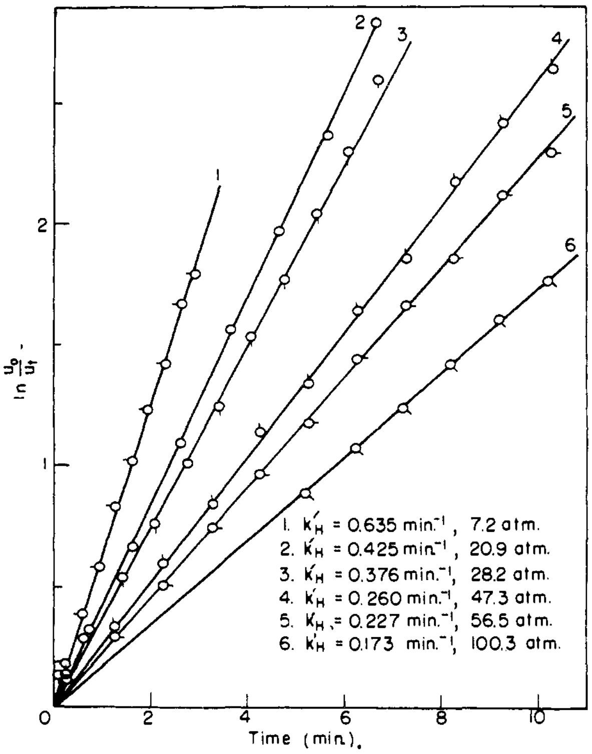

Fig. 3.—Ortho-para conversion in hydrogen on 0.237% Cr_2O_3–Al_2O_3 at 77°K. and various pressures.

column. The uncorrected rate constant k_H which was obtained from the slopes of the lines (Figs. 1, 2 and 3) are given in the fourth column. The half-lives calculated from rate constants corrected for the blank alumina runs (series 28) are shown in the fifth column. The number of moles of hydrogen delivered to the chamber is given in the sixth column.

Pressure Dependency.—The data for the 1.11×10^{-3} g.-atom chromium (0.0486% chromia–alumina) and 5.30×10^{-3} g.-atom chromium (0.237% chromia–alumina) at 77°K. plotted as half-life *vs.* pressure can be represented by two straight lines given approximately by the equations

$$\tau_{1/2} = 0.136p + 1.18 \text{ and } \tau_{1/2} = 0.0391p + 0.82 \quad (9)$$

respectively, as shown in Fig. 4.

Temperature Dependency.—For the 1.11×10^{-3} g.-atom chromium runs (Table II) a plot of half-life *vs.* $1/[T^{1/2}\,G(T)]$ as suggested by equation 8, shown in Fig. 5, at approximately 29.5 atm. can be represented by the solid straight line. The half-life values were corrected approximately to a pressure of 29.5 atm. by utilizing the first of equations 9.

Paramagnetic Site Dependency.—The rate data for runs (Table I) made at approximately 29 atm. and 77°K. are shown in Fig. 6 in which half-life is plotted against reciprocal site content C of the catalyst chamber.

Discussion of the Results

A summary of the rate data can be seen in Fig. 7 in which half-life *vs.* $p/[CT^{1/2}G(T)]$ is plotted. It is to be noted that while the plots of pressure and site content dependencies shown in Figs. 4 and 6 are made to test agreement with the general equation 7, the plot of the temperature dependency in Fig. 5 was of necessity made to correspond to the

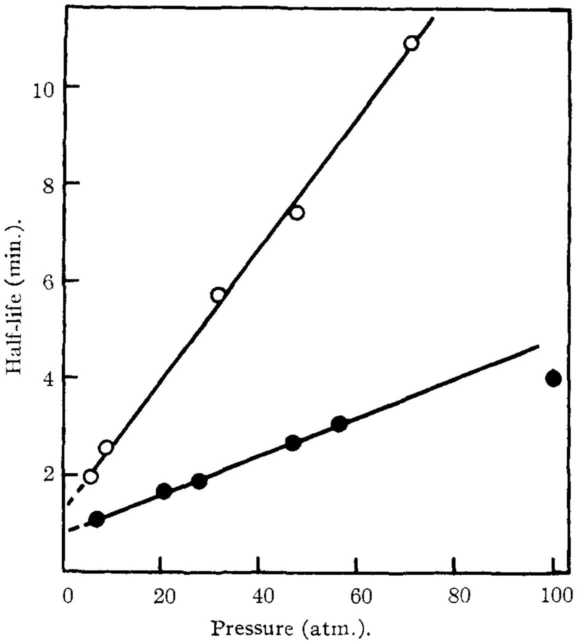

Fig. 4.—The effect of pressure on the ortho-parahydrogen conversion at 77°K. on 0.0486% chromia–alumina (open circles) and on 0.237% chromia–alumina (closed circles).

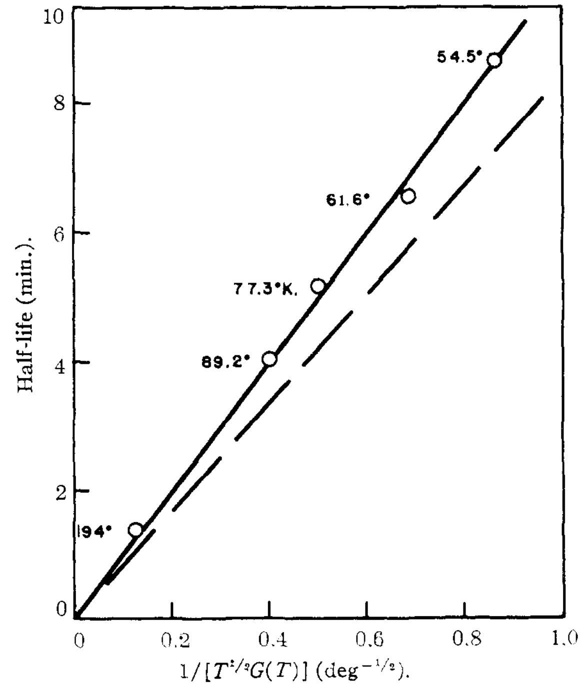

Fig. 5.—The effect of temperature on the ortho-parahydrogen conversion at approximately 29.5 atmospheres on 0.0486% chromia–alumina. The solid line represents the experimental data; the broken line was calculated from the absolute rate expression of Harrison and McDowell.[2]

high coverage case given by equation 8, since Q the activation energy of desorption is unknown.

TABLE I

SUMMARY OF RATE DATA, ORTHO–PARAHYDROGEN CONVERSION ON CHROMIA–ALUMINA AT 77°K.

Run	Cr in chamber, g.-atom $C \times 10^3$	Press. atm., p	Rate const., min.$^{-1}$ k'_H	Half-life,[a] min. $\tau_{1/2}$	H_2 in chamber, moles
28-2[b]	0.00	9.4	0.0106	..	0.27
28-1	.00	14.3	.0082	..	.40
28-3	.00	20.3	.0054	..	.56
28-4	.00	20.3	.0057	..	.52
26-10[c]	1.11	5.9	.360	1.99	.18
26-1[d]	1.11	7.9	...	..	..
26-9	1.11	9.2	.280	2.58	.28
26-4	1.11	31.6	.124	5.74	.81
26-3	1.11	47.8	.096	7.45	1.13
26-2	1.11	71.3	.065	10.94	1.66
27-5[e]	5.30	7.2	.635	1.11	0.20
27-1	5.30	20.9	.425	1.65	.50
27-2	5.30	28.2	.376	1.87	.68
27-4	5.30	47.3	.260	2.68	1.09
27-3	5.30	56.5	.227	3.08	1.27
27-6	5.30	100.3	.173	4.03	2.20
23-1[f]	6.93	28.0	.496	1.40	0.69
23-2	6.93	28.6	.496	1.40	.74
29-4[g]	14.32	9.2	.746	0.93	.28
29-3	14.32	14.4	.712	0.97	.43
29-1	14.32	25.0	.754	0.92	.63
29-2	14.32	30.3	.507	1.37	.79
24[h]	40.7	28.9	.604	1.15	.68
22[i]	46.7	30.6	1.05	0.66	.61

[a] Corrected for blank. Total catalyst chamber volume 202 cc. [b] 173.5 g. of unimpregnated leached carrier. [c] 173.5 g. of catalyst 19 CrAL of 0.0486% chromia–alumina. [d] Lost. [e] 170.0 g. of catalyst 21 CrAL of 0.237% chromia–alumina. [f] 174.5 g. of catalyst 4 CrA of 0.302% chromia–alumina. [g] 173.5 g. of catalyst 20 CrAL of 0.627% chromia–alumina. [h] 177.4 g. of catalyst 7 CrA of 1.74% chromia–alumina. [i] 143.6 g. of catalyst 2 CrA of 2.47% chromia–alumina in 163-cc. vol.

TABLE II

SUMMARY OF RATE DATA, ORTHO–PARAHYDROGEN CONVERSION ON 0.0486% CHROMIA–ALUMINA AT APPROXIMATELY 29 ATMOSPHERES[a]

Run	Temp., °K. T	Press. atm., p	Rate const., min.$^{-1}$ k'_H	Half-life, min. $\tau_{1/2}$	H_2 in chamber, moles
26-8	54.5	28.8	0.087	8.49	1.05
26-5	61.6	25.5	.122	5.84	0.83
26-4	77.3	31.6	.124	5.74	.81
26-7	89.1	28.5	.182	3.91	.59
26-6	194.5	29.5	.52	1.39	.25

[a] 173.5 g. of catalyst 19 CrAL of 0.0486% chromia–alumina.

The data in general support the theory of Harrison and McDowell; however it may be pointed out that the temperature dependency plot appears to intersect the origin (Fig. 5) while the plots of pressure and site content dependencies (Figs 4 and 6) do not. This appears to indicate an inconsistency between the data and theory. It would, of course, be desirable to make additional runs in which the temperature dependency was determined under various pressures and site contents.

Harrison and McDowell make a rough calculation of the absolute value of the rate constant k_H by assigning reasonable values to the variables in equation 6 and neglecting the pressure term in the denominator valid for the case of low surface coverage. Their calculated value compares well with their experimental value (5.1×10^{-3} and 3.1×10^{-3} min.$^{-1}$, respectively).

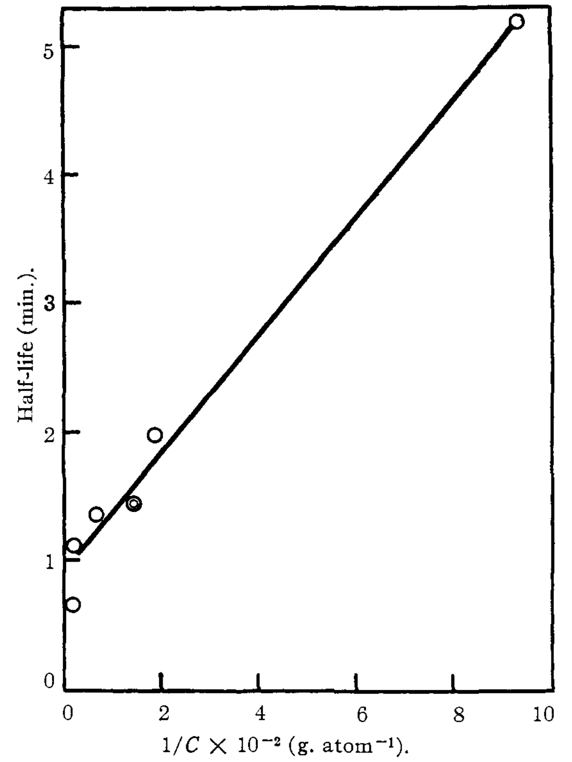

Fig. 6.—The effect of chromium content in chromia-alumina catalysts on the ortho-parahydrogen conversion at 77°K. and approximately 29 atmospheres.

While many of the variables appearing in equation 8 are not known with much accuracy, it was thought nevertheless of some value to make an absolute rate calculation using the same choice of the variables that Harrison and McDowell made in their calculation for the low coverage case. Harrison and McDowell used the following values: l^2/l_m was taken as 10^{-8} cm.; r_s was taken as 3 Å.; μ_a, the magnetic dipole equal to one Bohr magneton was 9.27×10^{-21} erg gauss^{-1}; μ_p, the proton magnetic moment, was 1/1840 Bohr magneton; s, the surface area, was 20 m.^{2}; v, the volume of the reaction vessel, was 200 ml.; T was 200°K.; a, the fraction of the surface active, was taken as 0.1; p was 10 cm.; θ, the fraction of the surface covered, was taken as 0.02; and ν, the number of molecules corresponding to a complete monolayer, was 10^{16} molecules cm.$^{-2}$. The calculated K from equation 3 was 3.3×10^{-48} c.g.s. units.[11]

The additional data necessary for an absolute rate calculation for the case of the ortho-parahydrogen conversion on 0.0486% chromia-alumina at 195°K. and 29.5 atmospheres are as follows: μ_{Cr}, the magnetic dipole moment for trivalent chromium using the spin only formula, is 3.87 Bohr magnetons[12]; $C = s\rho/N = 1.11 \times 10^{-3}$ moles trivalent chromium; v is taken as 120-cc. dead space volume; and the radius of an active center was taken as 2 Å. This last value was chosen by Harrison and McDowell for the radius of the paramagnetic site of a free radical and is adopted here for chromium for the purposes of this calculation. From the above the following is calculated: from equation 3, $K = 2.6 \times 10^{-48}$ c.g.s. units; using equations 4 and 5 together with the equilibrium para-ortho ratios[13] $T^{1/2}G(T) = 7.81$ deg.$^{1/2}$ and, finally, $\tau_{1/2} = 1.2$ min. The experimental half-life shown in Table II for run no. 26–6 is 1.4 min. The closeness of agreement is, of course, fortuitous in view of the accuracy with which the various values in the calculation are known.

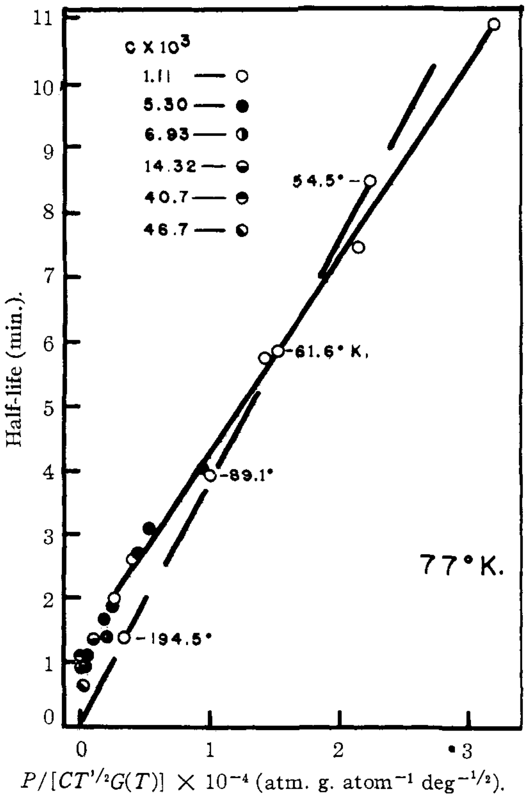

Fig. 7.—The effect of pressure, temperature and chromium content in chromia-alumina catalysts on the ortho-parahydrogen conversion.

For the case of 0.0486% chromia-alumina at 28.8 atmospheres and 55°K. the following is calculated: $T^{1/2}G(T) = 1.16$ deg.$^{1/2}$ and $\tau_{1/2} = 7.7$ min. The experimental half-life is shown in Table II for run no. 26–8: $\tau_{1/2} = 8.5$ min.

For the case of 0.0486% chromia-alumina at 71.3 atmospheres and 77°K., the following is calculated: $T^{1/2}G(T) = 2.00$ deg.$^{1/2}$, $s\rho/N = 1.11 \times 10^{-3}$ mole trivalent chromium in the chamber; $\tau_{1/2} = 11.5$ min. compared to an experimental value of 11.0 shown in Table I, run 26–2.

For 0.237% chromia-alumina at 100.3 atmospheres and 77°K., the following is calculated: $s\rho/N = 5.30 \times 10^{-3}$ g.-atom; $\tau_{1/2} = 3.5$ min. compared to an experimental value of 4.0 min. shown in Table I, run 27–6.

In Fig. 5 the dashed line represents the calculated half-life vs. $1/[T^{1/2}G(T)]$. It is seen that all the calculated half-lives are well within the variation which is possible in view of the eighth

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[11] It appears that K should be one half this value, making the calculated rate constant $k_H = 2.5 \times 10^{-8}$ min.$^{-1}$.

[12] J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford at the Clarendon Press, 1932, p. 285.

[13] A. Farkas, ref. 7, p. 14.

power dependency of r_s appearing in equation 8. The value $\nu = 10^{16}$ molecules cm.$^{-2}$ is undoubtedly high. From a consideration of the geometry of the closest packing of molecules on a surface Brunauer[14] gives for the area covered by one molecule

$$\text{Area} = (4)(0.866)\left(\frac{M}{4\sqrt{2}N_A\delta_l}\right) \qquad (10)$$

where M is the molecular weight of the gas adsorbed, δ_l is the density of the liquefied gas, and N_A is Avogadro's number. Taking the density of liquid hydrogen as 0.070 g. cm.$^{-3}$, the value $\nu = 7 \times 10^{14}$ molecules cm.$^{-2}$ can be calculated.

The significance of the calculations concerning the absolute rate is that the same choice of values for these variables gave agreement with experiment for both the low surface coverage case and the high surface coverage case, using different catalyst systems.

The agreement of the theoretical and experimental temperature dependencies both for the low surface coverage cases such as that investigated by Harrison and McDowell and for the higher surface coverage case investigated here, together with the pressure dependencies investigated for these two cases strengthens the model assumed in the theory for the conversion. This agreement is all the more striking in view of the fact that the theory predicts a negative temperature dependency for the low surface coverage case and a positive temperature dependency for the high surface coverage case.

It is a pleasure to acknowledge the assistance of Dr. Clarence M. Cunningham in the preparation of the catalysts and of Mr. L. E. Cox, foreman of the Cryogenic Laboratory Shop, in the construction of the catalyst chamber.

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[14] S. Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., 1945, p. 287.

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The Photolysis of Methyl Ketene

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RECEIVED DECEMBER 19, 1956

The gas phase photolysis of methyl ketene was investigated using light of 3650, 3130 and 2400 Å. wave length. The principal photolytic products were found to be CO, C_2H_4 and C_4H_8. The experimentally determined effects of temperature, wave length of light, methyl ketene and inert gas concentrations are explained by a mechansim involving vibrationally excited ethylidene radicals rearranging at measurable rates into ethylene. The alternative mechanism involving only photoexcited methyl ketene molecules is shown to be inconsistent with observations.

Introduction

Extensive investigations of the photolysis of ketene[2-7] have demonstrated the formation of the methylene radical and have provided some information on its kinetic behavior. The photolysis of the next homolog, methyl ketene, has not been described in the literature. By analogy, it should result in the formation of the ethylidene radical, CH_3CH. Previous attempts to study the chemistry of this radical have involved the pyrolysis and photolysis of diazoethane, CH_3CHN_2, and acetaldazine, $CH_3CHNNCHCH_3$. The decomposition of the latter was found to be quite complicated[8] and apparently does not involve the ethylidene radical to any important extent. Investigations of the properties of the ethylidene radical produced from diazoethane have been hampered by the hazards involved in handling this material.

Rice and Glasebrook[9] observed no reaction of the ethylidene radical with antimony mirrors when pyrolyzing diazoethane at 650° and higher. The only decomposition products detected were ethylene and nitrogen. The authors concluded that if ethylidene was formed at all under their conditions, it isomerized to ethylene so fast as to exclude all other reactions.

Barrow, Pearson and Purcell[10] observed the removal of selenium and tellurium mirrors when pyrolyzing diazoethane at 400°. As the furnace temperature approached 600° the rate of mirror removal progressively decreased, thus confirming the speculation of Rice and Glasebrook on the thermal instability of the ethylidene radical. The products resulting from the reaction with selenium mirrors were shown by Barrow, *et al.*, to have the properties of selenoacetaldehyde. The same product was obtained when the authors decomposed diazoethane photochemically in the presence of selenium mirrors.

The ultraviolet photolysis of diazoethane was also studied by Brinton and Volman[11] who detected small amounts of butene-2, hydrogen and acetylene among the products, in addition to ethylene and nitrogen. The authors suggested that butene-2 originated from the reaction

$$CH_3CH + CH_3CH \longrightarrow CH_3CHCHCH_3$$

Repeated explosions of diazoethane led to the discontinuation of this work. As the following will

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