cyclopentadiene is much lower. Hence it is both reasonable and significant that the electronic transitions in the two molecules should be so different in energy and probability of occurrence.

We wish to thank Drs. Emma P. Carr, Mary L. Sherrill and Hildegard Stücklen for their interest and assistance.

Summary

The ultraviolet absorption spectrum of 1,3-cyclopentadiene vapor between 32,000 and 66,000 cm.$^{-1}$ consists of a broad intense band with maximum at 43,000 cm.$^{-1}$ on which are superimposed narrow diffuse bands, and a group of sharply defined narrow bands beginning at 50,000 cm.$^{-1}$. Conclusions have been drawn regarding the oscillator strength of the broad band. Analysis of the vibrational structure of the discrete bands reveals at least two band systems with four prominent vibrational frequencies comparable to the totally symmetrical frequencies observed in the normal molecule.

The absorption spectra of solutions of cyclopentadiene and its dimer have also been measured.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Solid Free Radical as Catalyst for Ortho–Para Hydrogen Conversion[1a]

BY JOHN TURKEVICH AND PIERCE W. SELWOOD[1b]

Low temperature conversion of ortho–para hydrogen can be brought about by active charcoal, active metals and paramagnetic metallic oxides.[2] The catalytic effect of the above substances is ascribed in general to the effect of the inhomogeneous magnetic field of the paramagnetic catalyst on the physically adsorbed hydrogen. The theory of the magnetic conversion has been given by Wigner[3] and Kalckar and Teller.[4]

The object of the present investigation was to determine whether the list of solid substances catalytically active for this transformation could be extended to include solid free radicals. The latter due to their free unsaturated valence should give rise according to quantum theory to a paramagnetism of a definite magnitude. The organic free radical chosen for this investigation was α,α-diphenyl-β-picrylhydrazyl. This divalent nitrogen radical is rather easy to prepare, is highly dissociated in the solid state and is stable in air. The investigation consisted in the measurement of the magnetic susceptibility of the solid free radical to determine the extent of dissociation and in the measurement at liquid air temperatures of the hydrogen adsorption and the ortho-para hydrogen conversion rate on the free radical, zinc oxide and an intimate mixture of the free radical and the zinc oxide.

Materials

Zinc oxide was prepared by heating zinc oxalate in a muffle furnace at 400° until all visible decomposition ceased and then continuing the heating for ten hours at 450°.[5]

N-Nitroso-diphenylamine was prepared from diphenylamine according to the directions of E. Fischer.[6]

N,N-Diphenylhydrazine was prepared by reduction with zinc and acetic acid of the N-nitrosodiphenylamine.[6]

α,α-Diphenyl-β-picrylhydrazine was prepared from N,N-diphenylhydrazine and picryl chloride. It was recrystallized from ethyl acetate and had a melting point with decomposition of 172–173°.[7]

α,α-Diphenyl-β-picrylhydrazyl was prepared from the corresponding hydrazine by oxidation in chloroform solution with lead dioxide. It was recrystallized from hot chloroform and absolute ether.[7]

Hydrogen was tank hydrogen which was purified by passage over platinized asbestos at 300° and dried by calcium chloride, ascarite and phosphorus pentoxide.

1,1-ortho–para hydrogen was made by passing the above purified tank hydrogen over chromium oxide gel at liquid air temperature.

Zinc oxide–free radical mixture was made by grinding in a mortar equal weights of the two constituents.

Procedure

The magnetic susceptibilities were determined by the method of Gouy using the apparatus described by Selwood.[8] The measurements were carried out with mag-

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(1a) Presented at the St. Petersburg, Florida, meeting of the American Chemical Society in the spring, 1934.

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(2) Schwab, Taylor and Spence, "Catalysis," D. Van Nostrand Co., New York, N. Y., p. 213; Farkas and Farkas, "Light and Heavy Hydrogen," Cambridge Press, Cambridge, 1935, p. 89.

(3) Wigner, *Z. physik. Chem.*, **B23**, 28 (1938).

(4) Kalckar and Teller, *Proc. Roy. Soc.* (London), **A150**, 520 (1935).

(5) H. S. Taylor and D. V. Sickman, THIS JOURNAL, **54**, 602 (1932).

(6) Fischer, *Ann.*, **190**, 174 (1878).

(7) Goldschmidt, *Ber.*, **55**, 628 (1922).

(8) P. W. Selwood, THIS JOURNAL, **55**, 3161 (1933).

netic fields produced by currents up to 17.5 amperes. The relationship between the current and the field strength was established by calibration with distilled water for which the specific susceptibility at 20° was taken as -0.720×10^6 cgsm. units. The measurements were corrected for the small diamagnetic effect of the tube.

The adsorption and the ortho–para hydrogen conversion studies were made on an apparatus of the type used at Princeton for the study of gas adsorption.[9] It consisted of a gas purifying train, a gas buret compensated for variation in atmospheric pressure, a catalyst tube, a mercury manometer and a pumping system of a mercury two-stage diffusion pump backed by an oil pump. The gas burêt could be read with an accuracy of 0.1 cc. and the pressure reading to 1 mm. The temperature of the liquid air was determined by an oxygen vapor pressure thermometer. The dead space was determined with purified helium.

The rate of conversion of the ortho to para hydrogen was determined by introducing 70 cc. of purified tank hydrogen into the catalyst chamber, allowing the hydrogen to remain in contact with the catalyst for a definite time and then transferring by means of a Toepler pump a sample for analysis into the conductivity gage. The analysis was carried out by the thermal conductivity method developed by Bonhoeffer and Harteck.[10] The measurements were made in a Pyrex thermal conductivity vessel provided with a platinum wire 0.025 mm. in diameter and heated by a constant current from a 12 volt storage battery. The vessel was immersed in liquid air-bath. During the measurement the hydrogen was maintained at 40 mm. pressure and the wire temperature at about 170°K. where the two forms of hydrogen show a maximum difference in thermal conductivity. The wire temperature was measured in terms of its resistance by a Wheatstone bridge. The apparatus was calibrated with normal hydrogen (wire resistance of 42.94 ohms) and with 1:1 ortho–para hydrogen (wire resistance of 42.77 ohms). Because of the slow drift in the calibration values, analysis of the unknown mixture was sandwiched between these two determinations and the para content of the unknown was determined by linear interpolation.

Experimental Results

The results of the magnetic measurements are given in Table I.

TABLE I

Substance	T, °K.	$\chi_s \times 10^6$	$\chi_m \times 10^6$	$\chi_m \times 10^6$ cor.	p_B
Hydrazine		−0.51	− 201	....	..
Hydrazyl	273	+2.20	+ 869	+1070	1.62
	196	+3.21	+1268	+1469	1.64
	83	+7.26	+2868	+3070	1.71
ZnO (active)	273	−0.31			
	196	− .20			
	83	+ .62			
ZnO (ignited)	273	− .26			
	196	− .25			
	83	− .25			

The susceptibility of the hydrazine was found to be independent of the temperature and the molar value checked the value of 206 found by using Pascal's rule.[11] χ_m(cor.) was obtained by correcting the observed molal magnetic susceptibility χ_m for the diamagnetic contribution of the molecule which was taken as 201. p_B is the magnetic moment of the molecule in Bohr magnetons and was obtained using the formula

$$p_B = 2.84\, \chi_m(\text{cor.})\ (T - \Theta)^{12}$$

with Θ, the molecular field constant taken to be −37°K. as the best fit for our data on the temperature dependence of χ_m(cor.).

The value of $p_B = 1.73$ corresponds to complete dissociation of the tetrazine with the formation of two free radicals each with the resultant spin quantum number equal to one half. Therefore, our results clearly show that α,α-diphenyl-β-picrylhydrazyl not only is paramagnetic at liquid air temperatures but also exists completely as a free radical. Subsequent to our work Müller, Müller-Rodloff and Bunge[13] also found that this tetrazine was completely dissociated to give a radical with spin quantum number of one half. But their determination gave the value of Θ equal to −10°K.

The active zinc oxide was found to be slightly paramagnetic at liquid air temperatures. This paramagnetism was not due to paramagnetic impurity, for igniting the zinc oxide at 1000° for about twelve hours gave a product which was diamagnetic in the temperature range investigated. The paramagnetism could not be due to oxygen adsorbed at liquid air temperatures for the determinations of the magnetic susceptibility were carried out in a stoppered tube in an atmosphere of pure nitrogen. This paramagnetism is similar to that found by Hüttig[14] in the case of many "active" oxides. Undoubtedly, it is this small paramagnetism which is responsible for the small conversion of ortho–para hydrogen at low temperatures on zinc oxide.

The adsorption measurement of hydrogen on 19.8 g. of the free radical showed no adsorption at liquid air temperature. Zinc oxide (16.9 g.) and zinc oxide mixed with an equal weight of the free radical (19.8 g. with 19.8 g.) show appreciable hydrogen adsorption at liquid air temperatures as

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[9] H. S. Taylor and A. T. Williamson, THIS JOURNAL, **53**, 2168 (1931).

[10] Bonhoeffer and Harteck, *Z. physik. Chem.*, **4B**, 113 (1929).

[11] Stoner, "Magnetism and Matter," Methuen, London, 1934, p. 470.

[12] Stoner, *ibid.*, p. 477.

[13] Müller, Müller-Rodloff and Bunge, *Ann.*, **520**, 236 (1935).

[14] Hüttig, *Naturwissenschaften*, **20**, 640 (1932).

shown by Table II. The values obtained for hydrogen adsorption on zinc oxide are higher than those obtained by Taylor and Strother.[15]

TABLE II

ADSORPTION OF HYDROGEN ON ZINC OXIDE AT 85°K.

p, mm.	Cc. N. T. P. H_2/g. ZnO in absence of free radical	p, mm.	Cc. N. T. P. H_2/g. ZnO in presence of equal wt. of free radical
3	0.03	22	0.15
45	.17	38	.23
94	.51	63	.41
151	.73	116	.63
216	.97	157	.79
264	1.13	192	.95
316	1.30	235	1.20
391	1.53	275	1.39
448	1.70	338	1.66
512	1.85	422	1.98
588	2.03	472	2.15
653	2.19	535	2.36
766	2.41	590	2.48
		648	2.72
		694	2.82
		724	2.98

TABLE III

ORTHO-PARA HYDROGEN CONVERSION AT 85°K.

Free radical		Zinc oxide		Free radical on zinc oxide	
1 hr. 45 min.	14%	15 min.	2%	15 min.	84%
2 hr.	13%	35 min.	4%	30 min.	100%
4 hr.	25%	1 hr.	11%	1 hr.	100%
6 hr.	69%	2 hr.	20%		

The ortho-para hydrogen conversion is given in Table III.

It is seen that there is a slow conversion of the hydrogen on the free radical and a similarly slow conversion of the zinc oxide. Intimate mixing of the zinc oxide and the free radical produces a very rapid conversion. This is interpreted to mean that two factors are necessary for the heterogeneous catalysis of ortho to para hydrogen at low temperatures, namely, the existence of an inhomogeneous magnetic field, produced in this case by the free radical, and long contact of the hydrogen with this field, ensured by the van der Waals adsorption of hydrogen on the zinc oxide.

We wish to thank Professor Hugh S. Taylor for his interest in this investigation.

Conclusions

1. The magnetic characteristics of α,α-diphenyl-β-picrylhydrazyl, the corresponding hydrazine, active zinc oxide and ignited zinc oxide were determined.
2. Hydrogen adsorption at liquid air temperatures was determined on α,α-diphenyl-β-picrylhydrazyl, active zinc oxide and on an intimate mixture of the two.
3. Ortho-para hydrogen conversion at liquid air temperatures was found to be slow on zinc oxide and slow on the free radical but very rapid on an intimate mixture of the two.

PRINCETON, N. J. RECEIVED JANUARY 20, 1941

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[15] H. S. Taylor and C. O. Strother, THIS JOURNAL, **56**, 586 (1934).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

The Absorption Spectra of Ions of Europium and the Electric Fields within Some Coördination Compounds

BY SIMON FREED, S. I. WEISSMAN AND FRED E. FORTESS

No one examining the spectra of europium ions whether in solutions or in crystals would question that they represent for the most part the same kind of physical situations. The spectra consist of isolated groups of lines whose numbers, separations, and relative intensities vary with the ionic environment.[1] Not only does there appear a one-to-one correspondence in the groups of all these spectra but the wave lengths of the groups as a whole differ but little. When the crystals are anisotropic, the lines within each group usually possess different polarizations, a definite sign that the ions are oriented by the crystal fields. These fields can be thought of as having brought about a decomposition in the spectra somewhat as an external electric or magnetic field affects the line spectra of gases. As an electric field differs from a magnetic field in the pattern of the group it induces, so crystal fields of different symmetries would be expected, as a rule, to induce different patterns. We are then to ascribe the rather isolated groups appearing in the spectra

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[1] S. Freed and S. I. Weissman, *J. Chem. Phys.*, **6**, 297 (1938); S. Freed and H. F. Jacobson, *ibid.*, **6**, 654 (1938); S. Freed, S. I. Weissman, F. E. Fortess and H. F. Jacobson, *ibid.*, **7**, 824 (1939).