[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

The Use of the Ortho–Para Hydrogen Conversion in the Detection of Free Radicals Produced in Photo-dissociation[1]

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In considering the properties to be anticipated of the lighter free radicals which might be utilized to demonstrate their presence or absence in photochemical experiments, the paramagnetic properties which they should exhibit as the result of their possession of an odd electrom seem worthy of investigation. As, however, the low concentration of radicals to be expected in these experiments would make a direct determination of any change of susceptibility extremely difficult by ordinary magnetic methods, it was proposed to investigate the possibility of using the discovery of Farkas and Sachsse[2] that paramagnetic substances are capable of catalyzing the interconversion of ortho and para hydrogen for their detection. The method has already been used by Farkas and Sachsse in an investigation of the magnetic properties of B_2H_6,[3] and the possibility of its application to the problem considered here has also been stated by A. Farkas in his monograph.[4] If, for instance, methyl iodide vapor is dissociated by light to methyl radicals and iodine atoms in the presence of a mixture of ortho and para hydrogen which is not in equilibrium at the temperature of the experiment, the paramagnetic radicals should, during their period of free existence, be capable of changing the ortho–para ratio toward the equilibrium value, and the experimental finding of such a change could be taken as evidence of the production of paramagnetic substances, which, in this case, could scarcely be other than the methyl group or iodine atom. The result of absorption of radiation might also be the production of a molecule, without dissociation, in a paramagnetic excited state, which on collision with a hydrogen molecule might bring about conversion; but unless the excited state were metastable, its short life would cause such conversion to be negligibly rare in comparison with those brought about by the comparatively long lived free radicals.

Since the thermal conductivity method of Bonhoeffer and Harteck[5] will give false results for the ortho-para composition of a hydrogen mixture, if more than traces of gas other than hydrogen are admitted to the conductivity gage, it was necessary in these experiments, in which only liquid air was available as a refrigerant, to choose reactions in which the products contain little or no methane; carbon monoxide also is not removed by liquid air, but these experiments show that it can be fairly adequately removed by the usual cuprous-ammonium reagent. The production of molecular hydrogen is of course to be avoided, and also, as the conversion efficiency of hydrogen atoms is of the order of 10^6 times as great as that of substances effective in virtue of paramagnetic properties, the conversion in a reaction in which these are produced will mask that produced by other radicals. Methyl iodide, acetone, propionyl aldehyde and benzene were the substances examined.

Procedure

The platinum wire of the conductivity cell, spot welded to platinum leads, was 15 cm. long, 10 μ thick, with a resistance of some 50 Ω when carrying a heating current of 50 m. a. in hydrogen at 58 mm., the cell being immersed in liquid air maintained at constant level. In series with the wire was an accurate resistance of 50 Ω. From a measurement of the potential fall across this resistance by means of a Leeds and Northrup Student Type Potentiometer the current passing through the gage wire was calculated, and a measurement of the potential drop across the gage enabled its resistance to be determined. The heating current through the gage wire was made accurately the same for the different hydrogen samples required in a determination of the amount of conversion by adjusting a rheostat until a given potential difference existed across the standard 50 Ω resistance. Reproducibility of the gage resistance was usually within 0.01 Ω.

Dry hydrogen, freed from oxygen, from a 2-liter reservoir could be passed either directly to the gage ("ordinary" hydrogen, $o/p = 3/1$) or to the "converter" containing charcoal at liquid air temperature, where it was changed to approximately a 1:1 mixture ("converted" hydrogen). The converted hydrogen could be passed directly to the gage or bubbled through methyl iodide, etc., into the reaction vessel, a quartz tube 30 cm. long and 2.6 cm. in diameter, cemented to glass by silver chloride cement, and into a similar "blank" vessel (of glass, but with a silver chloride joint exactly like that in the reaction vessel) in

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[1] The results given here were reported at the meeting of the American Chemical Society held in New York, April 22–26, 1935.

[2] L. Farkas and H. Sachsse, *Z. physik. Chem.*, **B23**, 1 (1933).

[3] L. Farkas and H. Sachsse, *Trans. Faraday Soc.*, **30**, 331 (1934).

[4] A. Farkas, "Ortho-Hydrogen, Para-Hydrogen, Heavy Hydrogen," Cambridge University Press, 1935, p. 102.

[5] K. F. Bonhoeffer and P. Harteck, *Z. physik. Chem.*, **B4**, 113 (1929).

parallel with the reaction vessel. These vessels were filled to a total pressure of 1 atmosphere, the organic compounds being at a partial pressure equal to their vapor pressure at 20°. From these the contents could be passed through any necessary chemical absorbent and through a liquid air trap to the gage, which was filled by means of a capillary control to 58 mm. of mercury. The conversion was measured from gage resistance measurements in the presence of "ordinary," "converted," "illuminated" and "blank" hydrogen made immediately after one another. High vacuum technique was used throughout. Illumination was effected by two "cold" quartz mercury arcs 38 cm. long, placed as close as possible to the reaction tube, one consuming 300 watts at 3000 v., the other 500 watts at 5000 v. A large proportion of their luminous energy is at wave length 2537 Å. A fan directed on the arcs and reaction vessel kept the temperature practically that of the room. Radiation of wave length 1849 Å. was excluded by wrapping the reaction vessel in two layers of cellophane, 0.025 mm. thick.

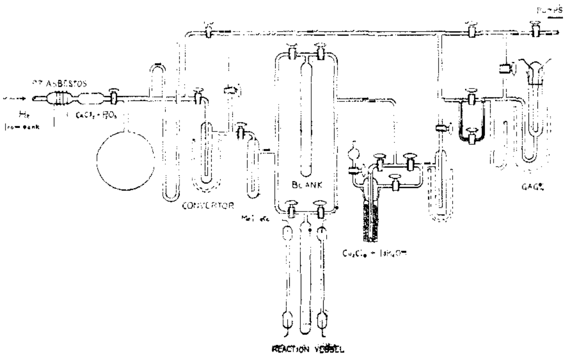

Fig. 1.—Reaction vessel.

Results

Preliminary experiments showed (a) a difference of about 1.8 Ω in the resistance of the gage wire in the presence of "ordinary" and completely "converted" hydrogen (b) a linear para-hydrogen concentration—resistance curve, (c) no change in the *o-p* ratio when a sample of converted hydrogen was left in the reaction vessel, without illumination, or in the blank overnight, whether in the presence or absence of methyl iodide vapor. Table I gives some representative results.

TABLE I

Substance	Exposure, min.	ΔR_1 ohms	ΔR_0	Corrected ΔR	% Conversion
Methyl	90	0.17	1.42	0.14	10
iodide	80	.21	1.79	.18	10 [a]
	225	.68	1.79	.60	34 [a]
	180	−.01	1.78		0[b]
Acetone	210	.60	.71	.31	44
	453	.90	1.03	.34	33
Propyl	187	.11	1.82	Probably	0
aldehyde	143	.12	1.15	0	0
Benzene	110	.20	1.21		?
	128	.12	1.80		?

[a] The bracketed data refer to the same run. [b] Illumination through glass.

ΔR_1 is the difference in the gage resistance immersed in "illuminated" and "blank" hydrogen, respectively, and ΔR_0 the corresponding difference for "ordinary" and "converted."[6]

Corrections.—Since the presence of only a few per cent. of methane or carbon monoxide in the gas which reaches the gage will give completely fallacious results, special experiments were carried out on methyl iodide and acetone to find how much carbonaceous material escaped the traps. Methyl iodide was chosen in the first place because, although it has a strong continuous absorption at 2537 Å., the actual decomposition effected by illumination is very small. The iodine recovered after two hours of exposure of methyl iodide and hydrogen under the same conditions as in the conversion experiments required only 2.49 cc. of 5×10^{-3} *N* thiosulfate for its titration, equivalent, if one atom of iodine is produced for every molecule of iodide decomposed, to the decomposition of rather less than 0.5% of the iodide initially present. To determine directly the amount of methane produced under the conditions of these experiments, the gas resulting from two hours' exposure of methyl iodide and hydrogen under the conditions of the conversion experiments was passed by means of a Töpler pump through a liquid air trap into a gas buret. This was analyzed by slow combustion in excess oxygen over a heated platinum spiral by Dennis' method, and the products passed into an absorption pipet containing an accurately known volume (some 5 cc.) of 0.02 *N* baryta. A turbidity was produced, showing the presence of carbon dioxide; the excess baryta was titrated by 0.01 *N* hydrochloric acid (microburet) and an apparent methane percentage of 0.46 was found in the hydrogen. Mercury was used throughout the gas analysis, as confining liquid. A blank experiment on the hydrogen, unmixed with methyl iodide, but otherwise treated in the same way as in the former experiment, also gave a turbidity with baryta, apparently arising from carbon compounds in the short pieces of connecting rubber tubing and stopcock grease in the gas analysis apparatus, equivalent to 0.34% methane, so that a methane con-

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(6) Values of ΔR_0 less than 1.8 Ω are due to a loss of efficiency of the charcoal in bringing about conversion to the low temperature equilibrium. After the introduction of air to the converter thorough baking out was found to be necessary to obtain a subsequent complete conversion to the 1:1 mixture.

tent of 0.12% is indicated in the hydrogen after two hours of illumination with methyl iodide.

The effect of this on the resistance of the gage wire can be estimated approximately in this way. From the calculated values of the rotational specific heats of ortho and para hydrogen at 93°K.,[7] one can calculate from the equation $\kappa = k\eta C_v$ the ratio of the thermal conductivities of 1/1 and 3/1 mixtures on the assumption that the viscosities are the same and that k is given by the somewhat uncertain equation[8]

$$k = {}^1/_4\,(9C_p/C_v - 5)$$

This ratio thus calculated is 0.963 for $\kappa(3/1):\kappa(1/1)$.

The thermal conductivity of hydrogen at 81°K. is given as 13.24×10^{-5},[9] and assuming this was for normal (3/1) hydrogen, the thermal conductivity for the 1/1 mixture is 13.77×10^{-5} and $\Delta\kappa = 0.53 \times 10^{-5}$. This corresponds to a difference in resistance in the gage wire of 1.79 Ω. In the experiment on methyl iodide in which an apparent change in resistance of 0.68 Ω was produced as the result of 225 minutes of illumination, 0.23% of methane might have been present in the hydrogen measured in the gage. The thermal conductivity of methane at 91.4°K. is given as 2.248×10^{-5},[10] and the conductivity of a mixture of 99.77% hydrogen (1/1) and 0.23% of methane would be 13.745×10^{-5}. The change in resistance in the gage wire produced by the presence of this amount of methane in the 1/1 mixture would be 0.085 Ω, compared with an observed change of 0.68 Ω, many times larger than could be accounted for by the production of methane. The change in gage resistance brought about in these experiments as the result of illumination seems attributable only to an actual change in the ortho–para ratio.

The acetone experiments were carried out with pure dry material in order to avoid the condensation reactions which take place in the presence of moisture.[11] The quantum yield in the photodecomposition of the vapor at wave length 26504 Å. is 0.33; half of the gaseous products consists of carbon monoxide and most of the rest of ethane; Damon and Daniels[11] report 10% of hydrogen in the product from the vapor, while Berthelot and Gaudechon[12] apparently from the photodecomposition of liquid acetone at the boiling point, find no hydrogen, but 5% methane in the products.

Removal of carbon monoxide by the cuprous ammonium complex ordinarily used for that purpose seemed the only method which would not disturb the ortho–para ratio, and the gas from the reaction vessel was slowly bubbled through a sludge of concentrated cuprous ammonium reagent and broken glass filling a trap between the reaction vessel and the liquid air trap. Special experiments showed that no conversion was brought about in this process. A direct determination of carbonaceous matter which escaped the traps, by the method previously described, showed the presence of 1.35% of such material estimated as methane or carbon monoxide as the result of three hours of exposure. The corrections have been made as before on the assumption that the interfering gas is methane; they would not be essentially changed if carbon monoxide were the disturbing substance. Although the corrections are considerable, there still remains a large resistance change in the gage as the result of illumination which cannot be accounted for by any methane or carbon monoxide possibly present.

Special significance is to be attached to the difference in the resistance changes produced by illuminating acetone and propionyl aldehyde, respectively. The quantum yield for the aldehyde decomposition of wave length 2537 Å. is about 1;[13] the principal products of decomposition are carbon monoxide and ethane, and an amount of hydrogen equal to 4% that of the carbon monoxide is reported. The products are of the same nature as and more in quantity than those from acetone; nevertheless, the observed change in resistance after illumination is only about one-sixth that produced by acetone. If the resistance change in the acetone experiments had been spurious, there would have been as large a change in the aldehyde experiments. The change of resistance observed in the aldehyde experiments is smaller than the corrections for the acetone experiments estimated as described above, and it seems very probable that it is entirely the effect of interfering material escaping the traps and that no appreciable ortho–para conversion is brought about by illuminated propionyl aldehyde. The

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(7) *E. g.*, K. F. Bonhoeffer and P. Harteck, *Z. physik. Chem.*, **B4**, 117 (1929).

(8) J. Jeans, "Dynamical Theory of Gases," Cambridge University Press, 1925, 4th ed., p. 302.

(9) Landolt–Börnstein, "Tabellen," 5th ed., Vol. II, p. 1305.

(10) Landolt–Börnstein, "Tabellen," 5th ed., Vol. II, p. 1306.

(11) G. H. Damon and F. Daniels, THIS JOURNAL, **55**, 2368 (1933).

(12) Berthelot and Gaudechon, *Compt. rend.*, **151**, 480 (1910).

(13) P. A. Leighton and F. E. Blacet, THIS JOURNAL, **54**, 3165 (1932).

magnitude of the correction to be subtracted from the observed change of resistance in the acetone experiments seems therefore overestimated rather than underestimated.

There is a small decomposition of benzene vapor on illumination by the mercury arc,[14] and if the products are the same as in the mercury-sensitized photo-decomposition, hydrogen and methane will be present. In any case, the observed change of resistance was relatively small, and probably is almost entirely to be attributed to uncondensable products.[15]

Discussion

The net result of these experiments is that the illumination of 1/1 ortho-para hydrogen mixture in the presence of methyl iodide and of acetone vapor at room temperature by light of wave lengths in the continuous absorption region of the organic compounds leads to a greater change in the thermal conductivity of the hydrogen than can be accounted for by the spurious presence of uncondensable gas; and the only reasonable interpretation is that appreciable conversion of the hydrogen mixture toward the room temperature equilibrium has been brought about. As, apart from solid catalysts and atomic hydrogen, the only substances known to bring about this conversion at an appreciable rate at room temperature are paramagnetic substances, the only conclusion to be drawn is that the organic substances under the action of the light gave paramagnetic entities capable of bringing about the conversion. That these were free radicals, or possibly, also, from methyl iodide, iodine atoms, allows of no reasonable doubt. The primary dissociation of methyl iodide in the region of continuous absorption into methyl radicals and iodine atoms can therefore be taken as certain.

The difference in the behavior of acetone and of propionyl aldehyde with respect to ortho–para conversion is completely in accord with the conclusions of Norrish[16] that photodecomposition of the aliphatic ketones occurs with the production of free radicals and of the aldehydes with a primary separation of carbon monoxide and formation of a saturated hydrocarbon. It seems certain from the experiments reported here that any free radical production on illumination of propionyl aldehyde is either much smaller or involves a much shorter life than in acetone under the same conditions. Although the experiments of Leermakers[17] point conclusively to the existence of a chain reaction in the photo-decomposition of acetaldehyde at high temperature and hence presumably to the presence of radicals, the "chain yield" at 25° is only 0.03 and, to quote this author, "It is possible that there are two modes of decompositions of aldehydes, one resulting in radicals, the other in carbon monoxide and hydrocarbon directly." Also, the experiments on the ortho–para conversion are in satisfactory agreement with those of Pearson,[18] who, employing the mirror methods of Paneth for the detection of free radicals, showed that mirrors could be removed by the products of illuminated acetone, and to a much less degree by those of propionyl aldehyde, and concluded that acetone exposed to light produces radicals and propionyl aldehyde does not.

Summary

An attempt has been made to detect the presence of free radicals in photo-dissociations by making use of the effect discovered by Farkas and Sachsse of the paramagnetic interconversion of ortho and para hydrogen.

Conversion in excess of any possible spurious effect was found to be produced by methyl iodide and acetone vapors illuminated to radiation of frequency in their continuous absorption regions, and not by propionyl aldehyde nor benzene.

The results are interpreted as indicating the production of paramagnetic free radicals on illumination of methyl iodide and acetone. The occurrence of conversion from acetone and not from propionyl iodide is strong evidence in support of Norrish's hypothesis of a difference in mechanism in the photo dissociation of aliphatic aldehydes and ketones.

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[14] J. R. Bates and H. S. Taylor, This Journal, **49**, 2450 (1927).

[15] The effect of benzene and of other hydrogen containing compounds reported by Farkas and Sachsse (*loc. cit.*) in bringing about ortho–para conversion is much too small to be detected in these experiments; that, for instance, methyl iodide itself does not bring about a conversion comparable to those noted here is shown conclusively by the blank experiments on methyl iodide, without illumination, and by the experiment on illumination through glass.

[16] R. G. W. Norrish, *Trans. Faraday Soc.*, **30**, 107 (1934).

[17] J. A. Leermakers, This Journal, **56**, 1537 (1934).

[18] T. G. Pearson, *J. Chem. Soc.*, 1718 (1934).