made up, and it may be advisable to redetermine which strength is best for the particular scheme of analysis being used.

Ammonium polysulfide prepared by the rapid method has been used successfully in this Laboratory over a period of three years for the separation of Divisions A and B in Group II.

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The Interaction between Methylene Radicals and Hydrogen

BY CHARLES ROSENBLUM

The photolysis of ketene in the presence of hydrogen points to a reaction between methylene radicals and hydrogen, in contrast with the relative stability[1] of methylene toward ketene itself and toward ether vapor. The reactants, 100 mm. of ketene and 225 mm. of hydrogen, were irradiated in a cylindrical quartz vessel (volume 130 cc.) by a "hot" mercury arc for about forty-five minutes, and the resultant gas mixture analyzed. Although a constricted arc was used throughout, a hydrogen–mercury vapor filter[2] for resonance radiation was interposed as an added precaution against the lamp as a source of hydrogen atoms. A mixture of ethylene and hydrogen did not react when exposed to the arc under these conditions.

Irradiation of ketene alone[3] results in an increase in volume due to the formation of carbon monoxide and ethylene as the sole gaseous products, this increase falling below the theoretical value after longer exposures because attendant polymerization creates a gaseous hydrocarbon deficiency. The reaction which occurs in the presence of hydrogen differs markedly from the above in that it is characterized by a volume decrease. This can be accounted for only if the gaseous hydrocarbon is saturated and some saturated liquid (or solid) hydrocarbons of low vapor pressure are formed, which implies a disappearance of hydrogen.

Analysis confirmed these expectations fully. Of the ketene decomposed in the presence of hydrogen at 35°, 1% yielded methane, 74% was recovered as a gas with an average composition[4] $C_{2.56}H_{7.12}$, and 25% yielded a residue of low volatility. At 200° the methane content corresponded to 9.6% of the decomposed ketene, the gaseous fraction with a mean composition[4] $C_{2.68}H_{7.36}$ represented 69%, and the residue accounted for 21% of the ketene present originally. In both cases, the average composition of the residual polymeric product was C_4H_{10}. The mean composition and quantity of this polymer were deduced from the carbon and hydrogen deficiencies in the balance sheet of initial and final gaseous components of the reaction system. The amounts of condensed product calculated in this manner agreed well with the observed volume decreases.

The experiments indicate that the direct association of methylene radicals and molecular hydrogen to form methane is inappreciable. The profound change in the nature of the products when hydrogen is present suggests that the interaction in question is

$$CH_2' + H_2 = CH_3 + H$$

Such a reaction yielding methyl radicals and atomic hydrogen would account for the formation of saturated and higher molecular weight hydrocarbons.[5] The methylene radical has been represented as energy rich (CH_2') since present accepted views as to bond energies would suggest that the reaction of a normal methylene radical with hydrogen would be endothermic. The energy of the radical must arise from the photoenergy absorbed during the dissociation process.

A secondary source of methyl radicals might be a reaction between methylene radicals and methane already formed

$$CH_2 + CH_4 = 2CH_3$$

This would be less endothermic than the reaction with hydrogen. The low yields of methane, increasing at higher temperatures, do not appear to support this view.

The source of methane is probably an interaction of methyl radicals with hydrogen[6] or hydrocarbons[7] which is known to take place readily at or above 150–160°. The recombination of methyl radicals to form ethane would account for the

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(1) Pearson, Purcell and Saigh, *J. Chem. Soc.*, 409 (1938).

(2) Morikawa, Benedict and Taylor, *J. Chem. Phys.*, **5**, 212 (1937).

(3) Norris, Crone and Saltmarsh, *J. Chem. Soc.*, 1533 (1933); THIS JOURNAL, **56**, 1644 (1934); Ross and Kistiakowsky, *ibid.*, **56**, 1112 (1934).

(4) Shown by cracking over a nickel catalyst in an excess of hydrogen.

(5) Summarized in Bonhoeffer and Harteck, "Grundlagen der Photochemie," Theodor Steinkopff, Dresden-Blasewitz, Germany, 1933, p. 264; also Jungers and Taylor, *J. Chem. Phys.*, **6**, 325 (1938).

(6) Cunningham and Taylor, *J. Chem. Phys.*, **6**, 359 (1938); Taylor and Rosenblum, *ibid.*, **6**, 119 (1938).

(7) Unpublished work of J. O. Smith, Princeton, 1938.

prominence of this constituent in the gaseous product.

Details of the temperature effect, which so far indicates a very small temperature coefficient for the photo-decomposition of ketene in hydrogen,[8] as well as the influence of varying concentrations of reactants and the addition of hydrocarbons, are being investigated.

[8] See also Ross and Kistiakowsky[3] in the absence of hydrogen.

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Potassium Acid Phthalate as a Buffer for Use with the Hydrogen Electrode

BY JOHN RUSSELL AND R. ELIOT STAUFFER

Several investigators[1] have reported in the literature that accurate measurements on 0.05 molar potassium acid phthalate cannot be made with the hydrogen electrode. On the other hand, Clark[2] states that repeated experiments have shown measurements on phthalate buffers to be reliable. Recently, MacInnes and co-workers[3] again have intimated that phthalate solution is unstable and cannot be measured satisfactorily with the hydrogen electrode, especially at 38°.

Our experience in this connection definitely supports Clark's statement, and, since the 0.05 *M* phthalate is so convenient a buffer for use in *p*H standardization, we are submitting the following data as evidence for the stability and reproducibility of hydrogen electrode potentials observed in it. We have used the following type of cell for *p*H measurements in these Laboratories (Pt) H_2; Solution X: 3.5 *N* KCl: 3.5 *N* KCl, satd. Hg_2Cl_2; Hg_2Cl_2; Hg, with 0.05 *M* phthalate as solution X in this cell both at 25 and 40°.

An essential feature in the design of the cell, which we hope to describe in detail later in connection with other studies, is the possibility of creating a very reproducible and constant junction between the potassium chloride bridge solution and solution X. Equally important in the obtaining of consistent and accurate measurements is the elimination of rubber connections in contact with the hydrogen supply or solution X, and the use of hydrogen prepared electrolytically in glass and passed over a hot platinum gauze catalyst in a fused silica tube. As a result, the cell in question has yielded highly reproducible and constant e. m. f. values with phthalate and other buffers. A few of these for phthalate at 40° are given in Table I.

TABLE I

ELECTROMOTIVE FORCE MEASUREMENTS OF POTASSIUM ACID PHTHALATE (0.05 *M*) WITH THE HYDROGEN ELECTRODE AT 40°

Reference half-cell	Phthalate soln.	E. m. f., v.	Date
A	1 X	0.49500	8-28-36
B	2 Y	.49504	9-21-36
B	2 Y	.49503	9-24-36
B	2 Y	.49496	9-28-36
B	3 X	.49503	9-25-36
B	3 X	.49501	9-28-36
C	4 Z	.49494	1-20-37
D	5 X	.49502	5- 5-37
	Average	.49500	

These measurements cover a period of about nine months during which four different calomel half-elements and bridging solutions were prepared, and five different phthalate solutions from three commercial sources of potassium acid phthalate were used. Each value in the table represents an average of values obtained by two or more platinum electrodes whose differences were rarely more than a few hundredths of a millivolt. Table II taken from a typical page of data shows that the e. m f. of the cell using phthalate as solution X remains substantially constant for periods as long as four hours after creating the liquid junction. The junction was formed as soon as the solution reached the temperature of the thermostat (*ca.* fifteen minutes).

TABLE II

CONSTANCY OF HYDROGEN ELECTRODE AND JUNCTION POTENTIALS WITH 0.05 *M* PHTHALATE BUFFER AT 40°

Hours after formation of junction	E. m. f., v.
0	0.49495
0.5	.49501
1	.49504
2	.49505
4	.49506

These data indicate that in our experience 0.05 *M* potassium acid phthalate can be used very satisfactorily as a buffer with the hydrogen elec-

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[1] I. M. Kolthoff and F. Tekelenburg, *Rec. trav. chim. Pays-Bas.*, **46**, 39 (1927); E. T. Oakes and H. M. Salisbury, THIS JOURNAL, **44**, 948 (1922); C. Z. Draves and H. V. Tartar, *ibid.*, **47**, 1226 (1925).

[2] W. Mansfield Clark, "The Determination of Hydrogen Ions," 3rd ed., The Williams and Wilkins Company, Baltimore, Md., 1928, p. 437.

[3] D. A. MacInnes, D. Belcher and T. Shedlovsky, THIS JOURNAL, **60**, 1099 (1938).