Experimental

Apparatus and Procedure for Tritiation of Multiple Bonds.—The tritiation apparatus employed is illustrated in Fig 1. The hydrogenation bottle containing catalyst and material to be tritiated was placed in a mechanical shaker. The entire system with stopcock E open was evacuated with a water aspirator through stopcock A and flushed several times with tank hydrogen through stopcock G. An atmosphere of "cold" hydrogen is left in the bottle by closing stopcock B. With the system evacuated at 15–20 mm. pressure, stopcocks C and F closed, and the mercury at the top of the 350-ml. buret at stopcock D, the tritium ampoule is opened at the break seal. The mercury in the buret is pulled down with the Toepler pump at the base of the buret in order to transfer the tritium from the ampoule into the buret. Stopcock D is then closed and the pressure in the ampoule brought to 1 atm. with tank hydrogen. The gas in the ampoule was then pulled into the buret and Toeplered back and forth between buret and ampoule twice to ensure thorough mixing. This process was repeated until about 150 ml. of gas at 1 atm. pressure was contained in the buret. The shaker was then started, and after this quantity of gas was used in the reduction, stopcock B was closed and the above procedure repeated. In all, this method of removal of tritium and reduction with portions of 150 ml. of gas was carried out five times. The buret was then filled completely with tank hydrogen and the reduction allowed to go to completion. The apparatus should be employed in an efficient hood and since once used for tritiation it becomes contaminated; thereafter, it should be used for tritiation experiments only.

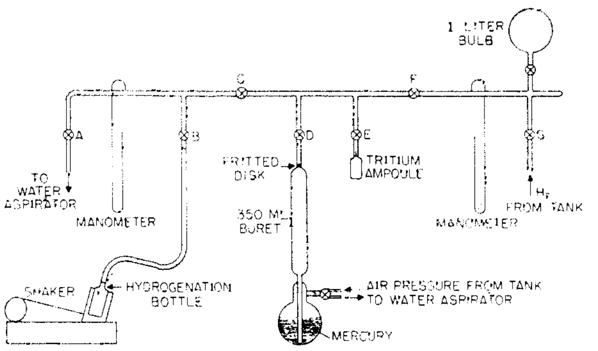

Fig. 1.—Tritiation apparatus.

Methylphenylcarbinol.—In a Parr hydrogenation bottle were placed 5.0 ml. of distilled acetophenone (b.p. 44–45°, 1 mm.) and 0.30 g. of platinum oxide catalyst. The reduction was carried out by the procedure described above employing a tritium ampoule containing 50 mc. (Oak Ridge value). The hydrogenation stopped by itself after 1158 ml. of gas was absorbed in 3.5 hr. (Theoretical uptake of hydrogen for reduction of acetophenone to carbinol was 1102 ml.). The organic material was dissolved in ether and filtered to remove the catalyst. After most of the ether had been distilled off at atmospheric pressure, the last traces were removed *in vacuo*. In a comparable cold run methylphenylcarbinol (b.p. 88°, 13.5 mm.) ($n_D^{25.5}$ 1.5260) was isolated in 92% yield.

Dehydration of Methylphenylcarbinol to Styrene.—In the hot run, the tritiated methylphenylcarbinol, after the last traces of ether had been removed from it, was dehydrated directly without distillation.

To the flask containing the methylphenylcarbinol were added 10 mg. of picric acid and 5 mg. of *p*-toluenesulfonic acid and to the receiver 10 mg. of picric acid. With the bath temperature at 155–190°, the water and styrene distilled at 42–68° at 100 mm. pressure. After drying over anhydrous magnesium sulfate, 3.54 g. of styrene b.p. (62.5–63.5°, 60 mm.) ($n^{27}D$ 1.5409) was obtained which represented a 79% yield based on acetophenone.

Analysis of this material for tritium indicated a specific activity of 0.66 mc./mm.

Oxidation of Styrene to Benzoic Acid.—In order to determine whether any tritium had been introduced into the styrene by exchange of tritium with protium on the benzene ring, the tritiated styrene was oxidized to benzoic acid with potassium permanganate[3] and the benzoic acid analyzed for its tritium content.

To remove any tritium that might have exchanged with the carboxyl hydrogen during the oxidation, the benzoic acid was dissolved in 5% sodium hydroxide solution and allowed to stand for 30 minutes. The solution was acidified with sulfuric acid and chilled in an ice-bath for 30 minutes. The white solid was filtered, washed with cold water and again dissolved in sodium hydroxide. This process was carried out four times in all. The benzoic acid thus obtained was dried in an Abderhalden pistol (m.p. 122.8–123.0°).

Analysis for tritium content indicated 0.06 mc./mm. which would correspond to 9% of the total tritium in the styrene.[4]

Tritium Analyses.—Analyses for tritium were accomplished by combustion of the organic compound on a semimicro scale and conversion of the tritiated water to tritium.[5] The tritium gas was then counted in an ionization chamber in conjunction with a Lindemann–Ryerson electrometer.[6] The equivalence of rate of discharge of the electrometer (mv./sec.) per millicurie of tritium was established with aliquots of tritium obtained by manometric dilution of several tritium ampoules of given activity as supplied by Oak Ridge National Laboratory.

Acknowledgment.—We wish to thank Mr. John J. Rohan for valuable assistance on the manometric dilutions of the tritium gas.

(3) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 164.

(4) If there were no preferential formation of C–T bond over C–H bond, then calculating from the values of the specific activities of the tritiated styrene and the tritiated benzoic acid, the specific activity of the carbinol should have been 1.26 mc./mm. Even if all of the 50 mc. of tritium in the ampoule had been introduced into the acetophenone, theoretically the maximum value of the specific activity of the carbinol would have been 1.16 mc./mm.

This observed discrepancy between the theoretical and computed values of the specific activity of the carbinol can be attributed to one or more of the following factors: (a) The values assigned by Oak Ridge for the tritium content of the 50 mc. ampoule and for several ampoules used in the standardization of the analytical procedure may have been in error. (b) The error of the analytical procedure employed is within ±5–10%. (c) There may be a preferential formation of the C–T bond or O–H bond over a C–H bond and O–T bond in the reduction of acetophenone with H–T.

L. C. Anderson and N. W. MacNaughton (This Journal, **64**, 1156 (1942)) have reported preferential formation of the C–D bond in the reduction of the carbonyl group with H–D over Raney nickel. However, they observed no such selectivity with a platinum catalyst at room temperature. They established that the observed effects were not due to exchange reactions under the conditions of the hydrogenation.

A preferential reaction of H–T with a carbonyl group would seem possible. If less than 100% of the tritium were introduced into the acetophenone, as is likely, the effect is even more significant. It is hoped that further work will help determine whether in catalytic reductions of carbonyl compounds with H–T such preferential formation of C–T bond actually occurs.

(5) F. C. Henriques, Jr., and C. Margnetti, *Ind. Eng. Chem.*, **18**, 420 (1946).

(6) C. D. Janney and B. J. Moyer, *Rev. Sci. Instruments*, **19**, 667 (1948).

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The Heat of Formation of Ferrocene

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Received June 6, 1952

Ferrocene has been prepared[1] by reaction of cyclopentadienylmagnesium bromide with ferric chloride, and also, by the direct action of cyclopentadiene on a "doubly-promoted Haber cat-

(1) T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

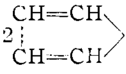
alyst."[2] A structure for ferrocene has been given previously[3] in which the iron atom is symmetrically situated between the planes of two cyclopentadienyl rings. This structure for ferrocene implies aromatic character and chemical evidence has been presented[4] for this character.

The heat of combustion of ferrocene has now been determined; the heat of formation calculated from this value and the chemical equation to which it applies are

$$10C(s) + 5H_2(g) + Fe(s) = (C_5H_5)_2Fe(s)$$

$$\Delta Hf^0_{298°} = +33.8 \pm 1.3 \text{ kcal.} \quad (1)$$

The heat of the following reaction has been calculated



$$2\left.\begin{array}{l}CH{=}CH\\ CH{=}CH\end{array}\right\rangle CH_2(l) + Fe(s) = (C_5H_5)_2Fe(s) + H_2(g) \quad (2)$$

$$\Delta H^0_{298°} = -17.4 \pm 1.4 \text{ kcal.}$$

The heat of formation of cyclopentadiene (+25.6 kcal.) was calculated using the heat of combustion of cyclopentane (786.54 kcal.)[5] and the heat of hydrogenation of cyclopentadiene (−50.9 kcal.).[6] The latter figure is for hydrogenation in the gas phase at 355°. The correction to 298° would be less than 0.05 kcal. and was therefore neglected. The standard states and additional thermochemical data used in calculations are those given in "Tables of Selected Values of Chemical Thermodynamic Properties," Natl. Bur. of Standards, 1947.

An attempt has been made to calculate the resonance and bonding energies in ferrocene. Since the energy of a C–H bond is 98.2 kcal.,[7] it can be assumed that ~100 kcal. would be required to break a normal C–H bond at 298°; the heat of recombination of the hydrogen atoms is −104 kcal. The resonance energy of the cyclopentadienyl radical was estimated in two ways. First, assuming that this radical with 5π electrons will be stabilized by resonance to $^5/_6$ the extent of the resonance stabilization in benzene (36 kcal.)[8] a value of 30 kcal. is obtained. A calculation by Dr. Richard Diamond, using a method analogous to the molecular orbital treatment for benzene,[9] gives a value of 1.83β. Again taking 36 kcal. for the resonance energy of benzene, making β equal to 18 kcal., a value of 33 kcal. is obtained for the resonance energy of the cyclopentadienyl radical. Since the actual value is more likely to be below than above either of these estimates, a value of 30 kcal. seems reasonable.

On the basis of the above we have

$$2C_5H_6 = 2C_5H_5\cdot + H_2 \qquad \Delta H = 36 \text{ kcal.} \quad (3)$$

The subtraction of equation (3) from equation (2) then gives 53 kcal. for the energy of the carbon to iron bonding. However, if one regards the total resonance energy for two cyclopentadienyl radicals, 60 kcal., as belonging to the ferrocene molecule as a whole (which is certainly more realistic), then the combined energies of resonance and carbon to iron bonding would be 113 kcal. An energy of this magnitude accords with the unusual stability of ferrocene.

TABLE I

WATER EQUIVALENT OF BOMB AND CALORIMETER

True mass, g.	Cor. temp. rise, °C.	Cal. from thread and eit	Wt. of water in pail, g.	Water equivalent	Dev. from mean, %
0.98146	2.7067	90.7	1904.87	424.9	+0.04
.94758	2.6094	78.6	1904.87	424.9	+ .04
1.00706	2.7760	88.6	1904.87	424.4	− .08
Mean				424.7	± .05

TABLE II

EXPERIMENTAL DATA ON FERROCENE

Sample	True mass, g.	Cor. temp. rise, °C.	Cal. from thread and eit	Fe_3O_4, g.	Fe_2O_3, g.	ΔH comb., kcal. mole^{-1}	ΔHf^0_{298} kcal. mole^{-1}
1	1.01703	3.3250	49.3	0.354	0.070	−1404.6	+33.9
2	0.99327	3.2640	85.2	.338	.077	−1404.3	+33.8
3	.97705	3.2055	83.5	.385	.021	−1402.2	+32.5
4	1.03915	3.4146	81.7	.375	.058	−1405.5	+35.1
Mean							+33.8

Experimental

The apparatus and procedure used were identical with those of Richardson and Parks,[10] with the following exceptions. The heat of combustion of the cotton thread (weighed in air) used for ignition was 4033 ± 3 cal. per g. The bomb was flushed by filling to 10 atmospheres pressure with oxygen and allowing this to escape until the pressure was again 1 atmosphere. Three repetitions of this procedure prior to each run sufficed to reduce the nitric acid correction, as determined by titration with standard base, to less than 0.05 calorie. The sensitivity of the bridge and galvanometer set-up was 0.00005 ohm (0.0005°). The mass of the material to be burned was determined to ±0.05 mg. and the weight corrected to vacuum. The water equivalent of the calorimeter and bomb were determined using U.S. Bureau of Standards benzoic acid (Sample 39F), and the measurements were made under the conditions specified by Washburn.[11] All temperature rises were corrected by the method of Dickinson.[12] The products of the combustion of the ferrocene are water, carbon dioxide, magnetic oxide of iron (Fe_3O_4) and ferric oxide. The percentage of iron present which was converted to Fe_2O_3 was in no case greater than 18%; calculation shows that in this range an error of ±2.0 in estimating this percentage produces an error of only 0.1 kcal. in the heat of combustion value. Furthermore, it is known that the heats of formation of the iron oxides are somewhat dependent upon the method by which they are prepared. An estimation of the Fe_2O_3 formed in combustion was made by washing it away from the Fe_3O_4 with water, since the Fe_2O_3 formed in a fluffy deposit over the inside of the bomb whereas the Fe_3O_4 remained largely in the small cup with a little spattered on the wall of the bomb in small adherent globules. A check chemical analysis of the oxides confirmed the above estimate of the amount of Fe_2O_3 formed in the combustion.

The ferrocene had been sublimed twice in a vacuum. Sample 1 was then recrystallized five times from carbon tetrachloride prior to use. Samples 2 and 3 were recrystallized three times prior to use. Sample 4 was recrystallized three times after sublimation and once immediately before use.

The mean value for $\Delta Hf^0_{298°}$ is 33.8 kcal. and the mean

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[2] S. A. Miller, J. A. Tebboth and J. F. Tremaine, *J. Chem. Soc.*, 632 (1952).

[3] G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, THIS JOURNAL, **74**, 2125 (1952).

[4] M. Rosenblum, M. C. Whiting and R. B. Woodward, *ibid.*, **74**, 3458 (1952).

[5] W. H. Johnson, E. J. Prosen and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 463 (1946).

[6] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, THIS JOURNAL, **58**, 146 (1936).

[7] K. S. Pitzer, *ibid.*, **70**, 2140 (1948).

[8] C. A. Coulson, "Valence," Oxford University Press, New York, N. Y., 1952, p. 235.

[9] H. Eyring, J. Wafter and G. E. Kimball, "Quantum Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 254.

[10] N. W. Richardson and G. S. Parks, THIS JOURNAL, **61**, 3543 (1939).

[11] E. W. Washburn, *Bur. Standards J. Research*, **10**, 525 (1933).

[12] H. C. Dickinson, *Bull. Bureau of Standards*, **11**, 189 (1914).

deviation is ±0.7 kcal. The estimated maximum error is ±1.3 kcal.

We wish to thank Professor G. B. Kistiakowsky for the loan of his equipment and for helpful advice, Mr. Irving Osvar for preparation of the ferrocene used in this experiment and Professor R. B. Woodward and Dr. R. M. Diamond for stimulating discussions.

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Identification of Phenols by Paper Partition Chromatography[1]

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RECEIVED MAY 19, 1952

A possible method of overcoming many of the difficulties often encountered in the paper partition chromatography of simple phenols was suggested in a recent paper[2] in which it was shown that if a mixture of phenols was allowed to couple with diazotized sulfanilic acid, the resulting mixture of phenylazobenzenesulfonic acid dyes could be satisfactorily chromatographed. The present paper describes a further study of the application of the above method to several series of isomeric and homologous phenols as well as other individual phenols. The compounds studied are listed in Table I in the order of their increasing migration coefficients.

Two-dimensional development as reproduced in Fig. 1 illustrates a satisfactory separation of *o*-cresol from *m*-cresol, and of *p*-methylguaiacol, 2,5-dimethylphenol and 2,4-dichlorophenol, although the migration coefficients of Table I would not indicate such to be possible.

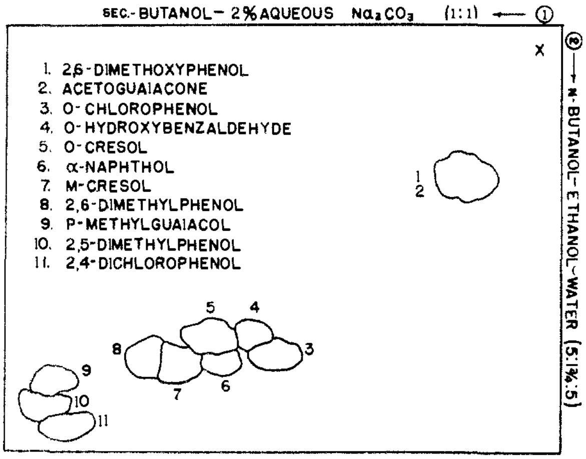

Fig. 1.—Two-dimensional chromatogram developed 40 hr. in each direction.

As a result of this study certain limitations of the method become apparent. Those phenols which

TABLE I

PHENOLS ARRANGED IN ORDER OF INCREASING MOBILITY OF THE PHENYLAZOBENZENESULFONIC ACID DYE[a]

	Color	Migration coefficient
Acetoguaiacone	Orange	0.11
2,6-Dimethoxyphenol	Pink	.12
Guaiacol	Orange	.19
Phenol	Yellow	.30
o-Chlorophenol	Yellow	.37
o-Hydroxybenzaldehyde	Yellow	.39
α-Naphthol	Pink	.43
o-Cresol	Yellow	.43
m-Cresol	Yellow	.43
2,6-Dimethylphenol[b]	Orange	.48
2,4-Dichlorophenol	Pink	.63
p-Methylguaiacol	Pink	.64
2,5-Dimethylphenol	Yellow	.66
o-Ethylphenol[b]	Yellow	.75
m-Ethylphenol[c]	Yellow	.76
p-Ethylguaiacol	Pink	.80
Eugenol	Pink	.81
3,5-Dimethylphenol	Yellow	.83
o-Phenylphenol	Yellow	.84
m-Phenylphenol	Yellow	.85
p-Phenylphenol	Pink	.86
p-Cresol	Pink	.89
2,3,5-Trimethylphenol[d]	Orange	.90
Dihydroeugenol	Pink	.93
3,4-Dimethylphenol	Pink	.94
β-Naphthol	Orange	.95
p-Ethylphenol[b]	Pink	.95
Thymol	Orange	.96
4-(α-Methylbenzyl)-2-phenylphenol[e]	Pink	.98
2,4-Dimethylphenol	Pink	.99
p-(α-Cumyl)-phenol[e]	Orange	1.00

[a] Prepared from two contiguous chromatograms irrigated 40 hr. with *s*-butanol-2% aqueous Na_2CO_3 (1:1 – v./v.). [b] Courtesy of Dr. J. J. McGovern, Mellon Institute. [c] Courtesy of Reilly Tar and Chemical Corp. [d] Courtesy of Shell Chemical Co. [e] Courtesy of Dow Chemical Co.

have a carbonyl function such as an aldehyde group para to the phenolic hydroxyl *may* react through replacement of the group by the entering azo group, thus destroying the identity of the original compound. Catechols because of their sensitivity to oxidation under alkaline conditions were not successfully chromatographed under the conditions thus far studied, in spite of attempts to prevent oxidation by replacement of the air in the chamber with an inert medium such as nitrogen. The presence of catechol interfered with the normal development of chromatograms of phenolic mixtures.

Experimental

The preparation of the dyes and the development of the chromatograms was carried out as previously described[1] with the exception that *s*-butyl alcohol which had been equilibrated with an excess of 2% aqueous sodium carbonate was used throughout on the one dimensional chromatograms. This solvent, although requiring up to 40 hours for full development, greatly decreased trailing and diffusion of spots. The presence of sodium carbonate in the equilibrated solvent helped prevent the formation of a second front which previously had often appeared as a result of temperature fluctuations in the developing chamber.[3]

Acknowledgment.—One of us (R.L.H.) wishes to express appreciation of a Grant-in-aid of Research

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(1) University of Minnesota Agricultural Experiment Station Scientific Journal Series Paper No. 2824. Abstracted in part from a thesis by Wen-Hua Chang presented to the Graduate Faculty of the University of Minnesota as partial fulfillment of requirements for the M.S. degree, June, 1951.

(2) R. L. Hossfeld, THIS JOURNAL, **73**, 852 (1951).

(3) E. L. Smith, *Nature*, **169**, 60 (1952).