The Detection of Free Radicals in Hydrogen Atom Reactions

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energies of benzene derivatives proves to be due to the use of incorrect bond-energy values. No special explanation in terms of differences in stability between cyclic and open-chain structures is necessary, since the required bond energies may be derived from open-chain compounds.

The bond energies in the normal paraffins reach constant values with increasing chain length. From Rossini's data[2] for the heats of formation of the paraffins, and values of 126.3 and 51.71 kcal. as the heats of formation per gram atom of carbon and hydrogen, respectively, in their standard states from monatomic gases at 298.1°K[3], the the C−C and C−H bond energies are found to be 60.3 and 87.1₅ kcal. The sum of these bond energies gives the heat of formation of *n*-hexane exactly, and using them we obtain 1407.6 kcal. for the heat of formation of cyclohexane from atoms, which is in very good agreement with the value of 1407.8 obtained from Rossini's data.[4]

With the above C−C and C−H values, that for the C=C energy may be obtained from Rossini's data[5] for the heats of formation of the monoölefin hydrocarbons, which were obtained by combining heats of hydrogenation with specific heat and heat of combustion data. For olefins with the double bond in the 1 position, this tends to a constant value of 101.2 kcal. With these bond energies, the apparent resonance energy of benzene is 41 kcal., in disagreement with hydrogenation result of 36. If, however, the heats of formation of the isomeric olefins are considered, and the other bond energies taken as constant, the C=C energy is found to vary from, for example, 101.3 in 1-henene to 107.2 in 2,3-dimethyl-2-butene. This is, of course, the well-known substitution effect noted by Kistiakowsky,[6] which persists to a considerable extent at 0°K.[7] The hexene in which the double bond most nearly resembles that found in an unsubstituted ring is clearly *cis* 3-hexene, for which the C=C energy is found to be 102.9 kcal. Using this C=C value, we obtain for the resonance energy of benzene 36 kcal. in agreement with the hydrogenation value. Similarly for 0-xylene, two of the C=C bonds may be taken as equivalent to that in 2-methyl-2-butene, and the third as equivalent to that in *cis* 3-hexene, which reduces the derived resonance energy by 12 kcal. to 34. Again, with Rossini's value for the heat of combustion of styrene,[8] and appropriate C=C energies obtained from non-cyclic compounds as before, the resonance energy of styrene obtained by the two methods agrees. That it is legitimate to consider the double bond in a ring structure as similar to a *corresponding* double bond in an olefin is shown by the fact that the heat of hydrogenation of non-cyclic compounds of the type CHR = CHR (*cis*) is the same as that of cyclohexene.

We should point out that while for convenience we have assumed that bond-energy differences are localized in the C = C bond, this is a purely formal treatment; some change may occur in other bond energies.

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The Detection of Free Radicals in Hydrogen Atom Reactions

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A LARGE number of investigations of reactions of hydrogen atoms with various substances have been made making use of the discharge tube method of Wood and Bonhoeffer.[1] With organic vapors, the mechanisms of such reactions have invariably been explained in terms of free organic radical chains.[2] However, no direct evidence for the existence of free radicals in such reacting mixtures has heretofore been reported. The Paneth-Rice technique for the detection of free radicals,[3] successfully applied in the past to photo-chemical and thermal decomposition reactions, has been recently adapted by the present authors to the hydrogen atom reaction problem.

A mirror of metal known to be insensitive to atomic hydrogen but sensitive to free organic radicals was deposited by condensation in a vacuum on a water-cooled glass finger, and introduced into the reaction chamber of the apparatus. Bismuth was adopted as the mirror metal in our work because of the ready availability (from uranium extraction residues) of its radioisotope of atomic weight 210, the activity of which is eminently suitable for tracer use. Preliminary experiments confirmed the non-removal of a radioactive bismuth mirror in the presence of atomic hydrogen alone, thus eliminating the possibility of the formation of a stable volatile hydride under the conditions of our experiments.

A volatile compound known to be easily decomposed at room temperature by atomic hydrogen, dimethyl mercury, was selected for trial. Previous work[4] had suggested a free radical mechanism to explain the products, which are free mercury and a methane-ethane mixture. It was readily demonstrated that no direct reaction occurred between the dimethyl mercury vapor and the bismuth mirror in the absence of atomic hydrogen within the temperature range 20° to 45°C. With the mirror maintained at 20°C, which was about 5° cooler than the prevailing room temperature, the presence of the hydrogen atom-dimethyl mercury reaction mixture resulted in a rapid clouding up of the mirror with condensed mercury vapor, and within a few minutes it was completely concealed by mercury droplets. Radioactivity measurements indicated that part of the bismuth was transported to a trap cooled in liquid air, some distance removed from the reactor, and recoverable from this trap as a volatile compound. However, after 20 minutes treatment most of the bismuth still remained on the cooled finger, apparently amalgamated with the mercury.

The experiment was repeated, this time maintaining the bismuth mirror at a temperature of 45°C. In this case, the mirror disappeared almost completely within the 20-minute reaction period, and the resulting volatile bismuth compound was shown to have been transported to the liquid air trap by means of radioactivity measurements, as before. The mercury formed in the reaction condensed as a grayish fog on the surrounding walls of the reactor, which were at

room temperature, and consequently about 20° cooler than the bismuth mirror.

Our experiments thus prove that a volatile bismuth compound, presumably the trimethyl, is formed when di-methyl mercury is decomposed by atomic hydrogen in the vicinity of thin deposits of metallic bismuth. The fact that the mercury produced in the reaction was prevented from amalgamating with the mirror metal when the latter was slightly warmer than the reactor walls, provides strong evidence that the dimethyl mercury-hydrogen atom re-action was a gas phase process, and not merely a hetero-geneous reaction on the surface of the bismuth deposit. The volatile bismuth compound must result, therefore, from direct reaction between alkyl radicals and the mirror. Full details of our technique and of correlative experiments now under way in this laboratory will be published else-where at a later date.

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Absorption by Hydrogen Sulfide in the 3.5μ–4.5μ Region*

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THE percent absorption by 90 cm of H_2S at 1-atmos-phere pressure is plotted against wave number in Fig. 1. This spectrum was obtained with a fluorite prism
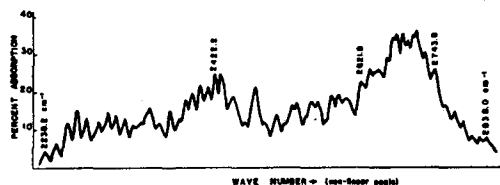

FIG. 1. Absorption by 90-cm atmos. of hydrogen sulfide in the 3.5μ–4.5μ region.

spectrometer which had a resolution of about 6 cm^{-1} in this region.

Theoretically, it is possible for three vibrational transi-tions (ν_σ, ν_π, and $2\nu_\delta$) to contribute to this absorption. It is especially noteworthy that considerable absorption is observed in the region 2620 cm^{-1} – 2450 cm^{-1}, where the P-branch of ν_σ may be expected to appear according to the calculations of Hainer and King,[1] but contrary to the reports of Nielsen and co-workers.[2]

A detailed tabulation of the absorption peaks at this resolution would be of little use unless accompanied by an analysis of the band envelope. A complete analysis will probably require new measurements at higher resolution.

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The Magnitude of the Experimental Error in the Adsorption of Nitrogen at 78°K on Various Surfaces

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THE adsorption isotherms of nitrogen at −195°C have been widely used in recent years to determine the sur-face areas of solids. The published values for the surface areas have covered the range from about 2000 square meters per gram to about 0.1 square meter per gram. If the surface area is large, a small sample of about one gram is sufficient in the experimental procedure for the adsorption measure-ments. However, for materials of small surface areas, it is necessary to take large samples and, hence, use adsorption tubes with comparatively large dead spaces. It is the pur-pose of this note to ascertain that part of the experimental error which may result from the use of the various sized adsorption tubes which are necessary to accomodate ad-sorbents of widely varying surface areas.

Assuming the perfect gas laws to apply to the gas phase measurements, the following expression gives the number of moles, n, of gas adsorbed for a given initial point in an adsorption measurement.

$$n = p_i V_B/300R - p_e V_B/300R - p_e V_D/78R, \qquad (1)$$

where p_i = initial pressure of nitrogen introduced into the buret system.

p_e = equilibrium pressure of nitrogen after exposure to sample at 78°K.

V_B = volume of nitrogen (S.T.P.) in the buret system.

V_D = volume of nitrogen (S.T.P.) in the dead space of the adsorption tube.

R = gas constant (in appropriate units).

Room temperature is taken as 300°K and the temperature of the liquid nitrogen as 78°K.

If δn be the variation in the number of moles adsorbed, then the general expression for the percentage error is:

$$\frac{100\delta n}{n} = 100 \left[\frac{\begin{array}{c}(V_B)p_i + (V_B - 3.85 V_D)\delta p_e \\ + (p_i - p_e)\delta V_B + (3.85 p_e)\delta V_D\end{array}}{V_B(p_i - p_e) - 3.85 p_e V_D} \right] \quad (2)$$

where δp_i, δp_e, δV_B, and δV_D are the corresponding varia-tions in p_i, p_e, V_B, and V_D, respectively. It is to be noted,

TABLE I.

	Sample (g)	B.E.T. Surface area (m²/g)	V_D (ml)	δV_D (ml)	Pressures (mm Hg) initial p_i	Pressures (mm Hg) equi-librium p_e	V_B (ml)	Percentage error $\frac{100\delta n}{n}$
Cement*	21.5	1.5	15.3	0.15	104.0	39.2	123.	1.1
Cotton*	31.1	0.7	121.	1.21	184.7	34.6	125.	10.4
Bone char (1)	1.92	121.	7.0	0.07	562.	156.	150.	0.20
Bone char (2)	1.92	121.	7.0	0.07	428.	0.4	47.	0.27
Glass spheres	12.29	0.93	16.3	0.16	232.8	67.6	50.1	1.9
Activated cocoanut shell charcoal	0.71	1720.	5.7	0.06	392.7	0.3	149.8	0.12
Titanium oxide	1.08	9.9	4.1	0.04	131.4	78.9	49.9	2.1

* Data kindly furnished through the courtesy of R. L. Blane of this Bureau.