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more detailed kinetics. However, a simple model, as here presented serves to explore the general outlines of flame stability behavior.

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¹ J. B. Rosen, *J. Chem. Phys.* **22**, 733 and 743 (1954).

² This result is based largely on very helpful suggestions made by Professor John von Neumann, Institute for Advanced Study, Princeton, New Jersey.

³ The coefficients $B > 0$, $D > 0$, and C are determined by the s.s. solution and are functions of z only. $-C$ is approximately the temperature derivative of the reaction rate and $\rightarrow 0$ as $z \rightarrow \pm \infty$ ($z = 0$ at s.s. temperature inflection point with gas flow from $-\infty$ to $+\infty$).

⁴ L. I. Schiff, *Quantum Mechanics* (McGraw-Hill Book Company, Inc., New York, 1949), Section 9.

⁵ In this, T = temperature, Y = product concentration, k = rate constant, $\phi = T/T_0$, $\sigma = E/RT_0$, and the subscript zero and ∞ refer to cold and hot conditions, respectively.

⁶ It should be noted that the limit occurs at a nonzero value of flame velocity.

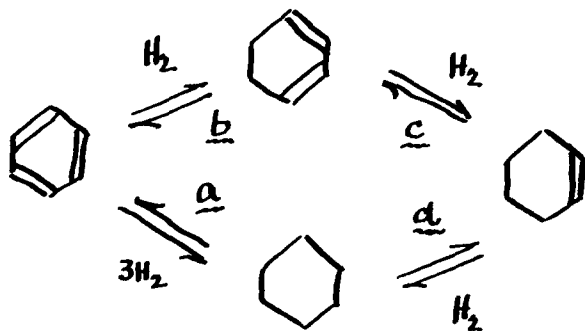
Thermodynamics of the Hydrogenation of Benzene

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THE hydrogenation of benzene in addition to the direct over-all reaction a to cyclohexane may be regarded as proceeding in three steps b , c , d , one for each mole of hydrogen added. Qualitative calculations on the equilibria in these systems



at 600°K have been reported by Taylor,¹ and direct experimental measurements of the over-all reaction equilibrium, by Burrows and Lucarni,² and Zharkov and Frost.³ In the present communication these are re-examined in the light of more recent thermodynamic data.

For benzene and cyclohexane, the thermodynamic data are well established.⁴ The statistical thermodynamic functions⁵ and experimental heat capacities^{6,7} for cyclohexene have also been reported.

The heat of combustion of cyclohexene has been recently measured by Pergiel and Prosen.⁸ Using these data [ΔH_c° (25°C) (liquid), -896.20 ± 0.17 kcal/mole, ΔH_f° (25°C) (liquid), -9.70 ± 0.19] and the heat of vaporization⁹ corrected to the present definition of the calorie, gives ΔH_f° (25°C) (gas), -1.72 ± 0.22 kcal/mole, for cyclohexene. A second value calculated from the heat of hydrogenation of cyclohexene to cyclohexane¹⁰ is -1.2 ± 0.1 kcal/mole. Of the two values, the former has been used in the present work. For cyclohexadiene no recent heat of combustion data are available. Using the heat of hydrogenation of cyclohexadiene to benzene,¹⁰ the heat of formation for cyclohexadiene, ΔH_f° (25°C) (gas), 25.6 ± 0.1 kcal/mole, was obtained.

The entropy of cyclohexadiene was estimated from that of cyclohexadiene.⁵ An increment of 5.3 eu accompanies the hydrogenation of one double bond in aliphatic olefins (e.g., *cis*-butene-1,3-butadiene, $71.90 - 66.62 = 5.28$; *cis*-2-pentene-*cis*-1,3-pentadiene, $82.76 - 77.5 = 5.26$). Accordingly the entropy of cyclohexadiene (assuming a symmetry number of 2) is 68.9 eu. The heat capacities were calculated by the method of Dobratz¹¹ using the tables of bonding frequencies reported by Stull and Mayfield.¹²

TABLE I. Thermodynamic data for benzene, cyclohexadiene, cyclohexene, and cyclohexane.

	$\Delta H_f^{298^\circ}$ kcal/mole	ΔS_{298° cal/deg/ mole	$C_p = a + bT^3 + cT^2$ (cal)		
			a	$b \times 10^3$	$c \times 10^6$
Benzene	19.82	64.3	-3.54	90.37	-36.67
Cyclohexadiene-1,3	25.6	68.9	-1.35	97.6	-37.3
Cyclohexene	-1.72	74.2	-9.14	131.9	-57.1
Cyclohexane	-29.43	71.3	-12.46	143.2	-54.94

The thermodynamic data for benzene, cyclohexane, cyclohexene, and cyclohexadiene are listed in Table I. The free energy changes were calculated using the modified form of the van't Hoff Isochore,

$$\Delta F_T^\circ = I_H + (\Delta a - I)T - \Delta aT \ln T - \frac{1}{2} \Delta b T^2 - \frac{1}{3} \Delta c T^3,$$

where the constants I_H and I_s are evaluated from the data at 25°C, and Δ signifies ($p - r$) for each property, and are summarized in Table II and Fig. 1. It follows that over the whole temperature range considered, cyclohexadiene is thermodynamically unstable relative to the other three compounds. The earlier prediction of

TABLE II. Change in free energy per molecule of hydrogen added in the hydrogenation of benzene.

Reaction	$T^\circ K$	400	550	700	1000
	298.16				
	ΔF (kcal)				
a^a	-23.40	-14.35	0.00	+13.62	+41.97
b	13.2	15.7	19.6	23.5	31.3
c	-17.9	-14.8	-10.2	-5.5	+4.2
d	-18.7	-15.2	-9.4	-4.4	+6.5

^a For the over-all reaction, the free energy tables in reference 4 were used.

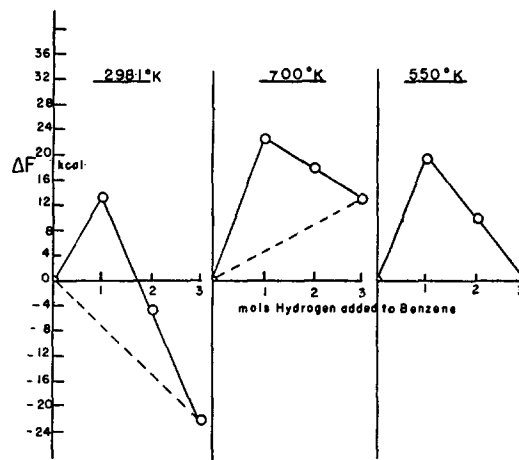


FIG. 1. Thermodynamic free energy change in the hydrogenation of benzene per molecule of hydrogen added.

Taylor at 600°K based on very qualitative calculations, is in accord with these results. It has been known experimentally for a long time that cyclohexadiene and cyclohexane react to form benzene and cyclohexane even by passage through heated tubes without any catalysts. It is clear from the thermodynamic conclusions that at moderately high temperatures, cyclohexadiene and cyclohexene could never be isolated, even in trace amounts in the hydrogenation of benzene.

A comparison of the results reported by Burrows and Lucarni² and Zharkov and Frost³ by direct measurement in this temperature region with the values calculated using precise thermodynamic data is shown in Fig. 2. The free energy change, from the data of Burrows and Lucarni, is -23.43 kcal/mole at 25°C, whereas the value calculated thermodynamically is 23.40 kcal/mole. The agreement leaves little to be desired, especially in view of the various difficulties in the direct experimental measurement of equilibrium data.

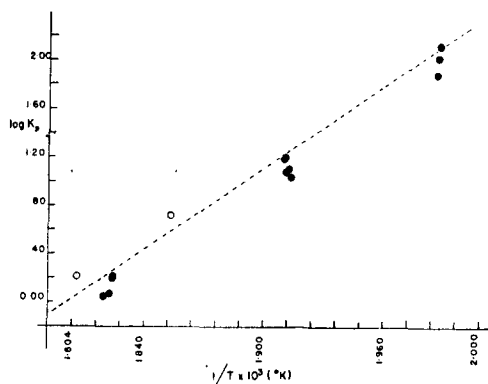


Fig. 2. Comparison of experimental data and thermodynamic values for the benzene-cyclohexane hydrogenation reaction at equilibrium. ○ G. H. Burrows and C. Lucarni, *J. Am. Chem. Soc.* **49**, 1157 (1927). ● V. R. Zharkov and A. V. Frost, *J. Gen. Chem. U. S. S. R.* **2**, 534 (1932). --- Values predicted thermodynamically from data in reference 4.

The author thanks Dr. E. J. Prosen for his very helpful comments on these calculations, and for the most recent data on cyclohexene prior to publication.

- ¹ H. S. Taylor, *J. Am. Chem. Soc.* **60**, 627 (1938).
- ² G. H. Burrows and C. Lucarni, *J. Am. Chem. Soc.* **49**, 1157 (1927).
- ³ V. R. Zharkov and A. V. Frost, *J. Gen. Chem. U. S. S. R.* **2**, 534 (1932).
- ⁴ "Selected Values of Properties of Hydrocarbons," Circular Natl. Bur. Standards, C461, U. S. Dept. Commerce, Washington, D. C. (1947).
- ⁵ Beckett, Freeman, and Pitzer, *J. Am. Chem. Soc.* **70**, 4227 (1948).
- ⁶ Huffman, Eaton, and Oliver, *J. Am. Chem. Soc.* **70**, 2991 (1948).
- ⁷ J. B. Montgomery and T. DeVries, *J. Am. Chem. Soc.* **64**, 2375 (1942).
- ⁸ F. V. Pergiel and E. J. Prosen, National Bureau of Standards Thermochemical Laboratory, unpublished data.
- ⁹ J. H. Mathews, *J. Am. Chem. Soc.* **48**, 562 (1926).
- ¹⁰ Kistiakowsky, Ruhoff, Smith, and Vaughan, *J. Am. Chem. Soc.* **58**, 137 (1936).
- ¹¹ C. Dobratz, *Ind. Eng. Chem.* **33**, 759 (1941).
- ¹² D. R. Stull and F. D. Mayfield, *Ind. Eng. Chem.* **35**, 639 (1943).

The Radical Pair Yield of Ionizing Radiation in Sulfuric Acid Solution*

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SOLUTIONS of ceric sulfate in 0.8*N* H₂SO₄ were irradiated in the presence and absence of various gases under two different conditions: In one case the gases were constantly bubbled through the solution under irradiation (flow system), while in the other, the solutions were initially saturated with the gas (CO and air only) and then irradiated (static system). In both the flow and static systems Ce⁴⁺ analyses were performed; however, gas analyses were also done in the static system.

Flow system.—Ceric sulfate solutions (10⁻¹–10⁻³M in 0.8*N* H₂SO₄) were irradiated in the presence of N₂, He, H₂, air, and CO, in a cylindrical CO⁶⁰ source. Highest-purity tank gases were used when possible and these were further purified by passage through an appropriate gas train. Carbon monoxide, made by the method of Thompson,¹ was carefully purified and found to contain less than 0.5 percent of fixed gases (O₂, N₂, H₂) and no hydrocarbons, by mass spectrographic analysis. The gases were bubbled through the solution (flow rate 300 cc/min) during irradiation and the solution analyzed at various intervals. All solutions were carefully preflushed before irradiation. Since sources of different intensity were used, all results have been normalized to a constant dose rate of 3576 ± 36 μM of air sat FeSO₄ oxidized/hr. The results are summarized in Fig. 1. In the presence of CO or H₂ the rate of Ce⁴⁺ reduction was 1190 ± 12.5 μM/hr and 1202 ± μM/hr, respectively. In the presence of air, N₂, or He the rate of Ce⁴⁺ reduction was 601 ± 6.1, 596 ± 4.0, and 595 ± 6.3 μM/hr, respectively.

Static system.—In Fig. 2 is summarized the rate of CO₂ formation obtained by irradiating solutions of 0.8*N* H₂SO₄ (with and without added Ce⁴⁺) initially saturated with CO at 300–500*m* pressure, with hard x-rays (dose rate 234.5 μM Fe oxid/1000 sec).

These solutions were prepared by variation in a method previously described.² The method consists essentially of saturating a

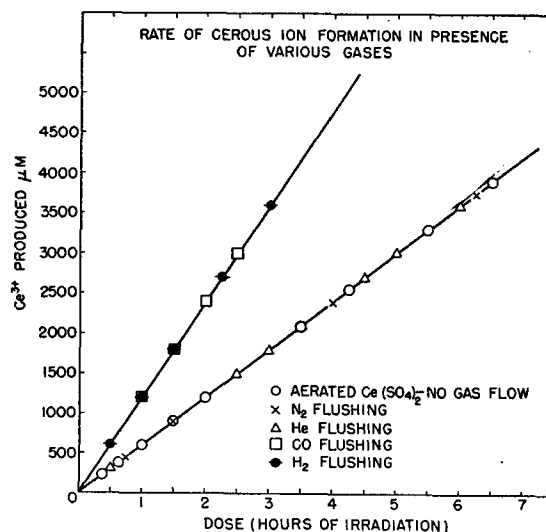


FIG. 1.

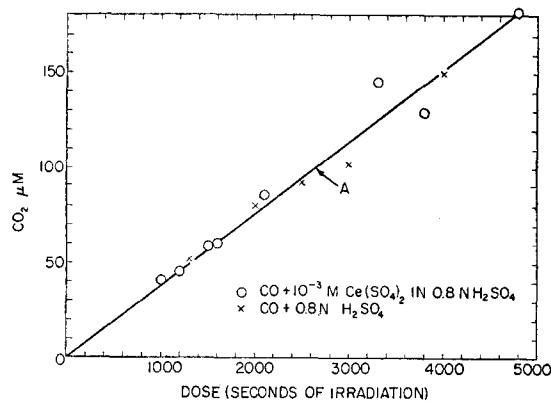
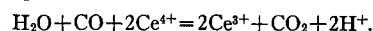


FIG. 2.

de-aerated solution with CO and pouring this solution into 10-cc bulbs sealed to a manifold with 4-mm heavy walled tubing, partially evacuating and then sealing off the bulbs. Curve A, Fig. 2 is the normal rate of ceric sulfate reduction (aerated and de-aerated mM solutions of Ce(SO₄)₂ in 0.8*N* H₂SO₄) and is equal to 38.0 ± 1.9 μM Ce⁴⁺ reduced/1000 sec. The rate of CO₂ formation from all solutions was 38.3 ± 1.8 μM/1000 sec. The rate of Ce⁴⁺ reduction in the presence of CO, in this system was 75.5 ± 1.5 μM/1000 sec. These results indicate the following stoichiometry for the reduction of Ce⁴⁺ in the presence of CO:



From these results it would appear that the molecular H₂O₂ formed in reaction (1) is either destroyed or does not exist as such. We believe that these data can be explained by assuming the following reactions:

