large,[9] therefore moments calculated from ($P - R_D$) should always be critically examined in light of the structure of the particular molecule.

The value of 1.18 $D$ obtained for unpurified ether (A) indicates that some of the previous data (Fuchs and Stuart, Table III, *e* and *h*, respectively) may be based on a sample of ether that contained a significant amount of polar impurity and that the agreement of these authors values with the others recorded may be fortuitous.

The value 1.22 $D$ for methyl ethyl ether falls between 1.14 $D$ for diethyl and 1.30 $D$[10] for dimethyl ether.

A comparison of the observed moment with that calculated for vector addition for the *o*-, *m*- and *p*-halogen toluenes is given in Table IV. The bond moments used were: $C_{ar}$–$CH_3$ (vapor) = 0.37, $C_{ar}$–$CH_3$ (solution) = 0.39, $C_{ar}$–F(vapor) = 1.61, $C_{ar}$–Cl (solution) = 1.56, $C_{ar}$–Br (solution) = 1.53 and $C_{ar}$–I (solution) = 1.38. The bond moment values for solution are taken from Tiganik,[11] the vapor $C_{ar}$–$CH_3$ from Baker[12] and the 1.61 for $C_{ar}$–F from the present investigation.

TABLE IV

ELECTRIC MOMENTS (DEBYES)

| Substance | Ortho Calcd. | Ortho Obs. | Meta Calcd. | Meta Obs. | Para Calcd. | Para Obs. |
|---|---|---|---|---|---|---|
| Fluorotoluene (vap.)[a] | 1.46 | 1.35 | 1.82 | 1.85 | 1.98 | 2.01 |
| Chlorotoluene (sol.)[b] | 1.41 | 1.43 | 1.79 | 1.77 | 1.95 | 1.94 |
| Bromotoluene (sol.)[b] | 1.38 | 1.44 | 1.76 | 1.75 | 1.92 | 1.93 |
| Iodotoluene (sol.)[c] | 1.24 | 1.33 | 1.61 | 1.67 | 1.77 | 1.80 |

[a] Present investigation. [b] Reference 11. [c] H. Poltz, *Z. physik. Chem.*, **B20**, 351 (1933).

Deviation from vector addivitity ~ 0.1 debye occurs only for *o*-fluoro- and *o*-iodotoluenes and these are in opposite sense to each other. Until data for the chloro-, bromo- and iodo-toluenes in the vapor phase is available it is felt that a discussion of such deviations as exist is of limited value and would necessarily be somewhat speculative.

## Summary

The electric moments of several organic molecules have been determined from gas phase measurements of the dielectric constant at several temperatures and pressures. The results in debyes are: fluorobenzene—1.61, chlorobenzene—1.70, *m*-difluorobenzene—1.58, *o*-dichlorobenzene—2.54, *o*-fluorotoluene—1.35, *m*-fluorotoluene—1.85, *p*-fluorotoluene—2.01, diethyl ether—1.14 and methyl ethyl ether—1.22.

DURHAM, N. C. RECEIVED SEPTEMBER 13, 1948

[9] (a) Coop and Sutton, *J. Chem. Soc.*, 1269 (1938); (b) Finn, Hampson and Sutton, *ibid.*, 1254 (1938).

[10] Sanger, Steiger and Gachter, *Helv. Phys. Acta*, **5**, 200 (1932). The value 1.29 given by these authors is raised to 1.30 when the new value of $N_A$ is used.

[11] L. Tiganik, *Z. physik. Chem.*, **B13**, 425 (1931).

[12] Baker and Groves, *J. Chem. Soc.*, 1144 (1939).

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[CONTRIBUTION NO. 61 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

# The Catalytic Hydrogenation of the Benzene Nucleus. V. The Hydrogenation of Benzene, the Cyclohexadienes and Cyclohexene

BY HILTON A. SMITH AND HENRY T. MERIWETHER

## Introduction

It is a well known fact that the benzene nucleus is hydrogenated with considerably greater difficulty than a simple unsaturated system. This is presumably due to the large resonance energy of the benzene ring system. If this is the case, one would expect the conjugated 1,3-cyclohexadiene to hydrogenate less readily than either the unconjugated 1,4-cyclohexadiene or cyclohexene. In order to test this, a study of the rates of hydrogenation of cyclohexene, the cyclohexadienes, and benzene was undertaken.

## Experimental

Merck reagent thiophene-free *Benzene* was purified by fractionation in an 8-ft. Vigreux column. The fraction used for rate studies distilled at a temperature of 79.2° at 741 mm., and had a refractive index, $n^{20}$D, of 1.5003.

Eastman Kodak Co. technical *cyclohexene* was first distilled through the 8-foot column and the fraction boiling between 81.8 and 82.0° collected. This was mixed with an equal volume of methanol, and azeotropic fractionation carried out in the same column. The fraction boiling at 55.8° was washed five times with cold water in order to remove the methanol, and dried with anhydrous magnesium sulfate. Fractionation of this product gave a constant boiling cut with a head temperature of 81.8° at 738 mm. pressure; $n^{20}$D was 1.4458.

1,3-Cyclohexadiene and 1,4-cyclohexadiene were prepared by dehydration of quinitol according to the method of Zelinskii and co-workers.[1] Quinitol was prepared by the reduction of hydroquinone over Raney nickel at 150° and 2,000 p. s. i. hydrogen pressure. The solvent, ethanol, was removed from the hydrogenated product by distillation and the quinitol recrystallized from acetone. The quinitol was then dehydrated by heating with potassium bisulfate in a stream of carbon dioxide gas. The hydrocarbon and water were condensed in a cold-finger containing a little hydroquinone, to prevent polymerization. The hydrocarbon layer was separated, washed with sodium bicarbonate, and distilled from a simple distilling flask. The fraction boiling between 75 and 125° was again washed with sodium carbonate solution, dried over potassium carbonate, mixed with an equal volume of methanol, and fractionated in an 8-ft. Vigreux column. Three fractions were collected, washed five times with cold water, dried over anhydrous potassium carbonate, and refractionated. Two constant boiling cuts were obtained. The 1,3-cyclohexadiene distilled at 79.3° at 738 mm., and had

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[1] Zelinskii, Denisinka and Eventova, *Compt. Rend. Acad. Sci. U. S. S. R.*, **1**, 313 (1935).

a refractive index, $n^{20}\text{D}$, of 1.4746.[2] The 1,4-cyclohexadiene distilled at 88.3° at 738 mm.; $n^{20}\text{D}$ was 1.4720.[3]

The acetic acid solvent was prepared by fractionation in a five-foot helix-packed still. The platinum catalyst was prepared by standard methods.[4] The hydrogenations were carried out in a standard low-pressure Parr catalytic reduction apparatus. The volume of the hydrogen reservoir, reaction bottle, and connections during hydrogenation was 4.43 liters. The reaction bottle was equipped with a brass jacket through which water at any desired temperature could be circulated from a twenty-liter reservoir. At the start of each run, the solvent, hydrocarbon, and catalyst were placed in the reaction bottle which in turn was placed in the water jacket and allowed to attain the temperature of the circulating water before being fitted into the rocking cradle of the apparatus. The reaction was then started in the usual manner.[5] The temperature inside the bottle was taken at the end of the hydrogenation. Usually a slight rise was found. This was caused by the heat evolved during the course of the reaction. In all cases the amount of hydrogen absorbed corresponded to that necessary for complete hydrogenation of the ring.

## Experimental Calculations and Results

It was established that all of these hydrogenations were first order with respect to hydrogen pressure, zero order with respect to the concentration of hydrogen acceptor, and directly proportional to the amount of catalyst used. This is demonstrated by Table I. Therefore rate constants were calculated from the equation

$$\log \frac{\overset{\circ}{p}_{H_2}}{p_{H_2}} = \frac{kt}{2.303V}$$

by plotting $\log \overset{\circ}{p}_{H_2}/p_{H_2}$ against $t$, and multiplying the slope of the line thus obtained by $2.303V$.[6] These constants all referring to one gram of standard catalyst[5] are given in Table II together with the energies of activation for the hydrogenation.

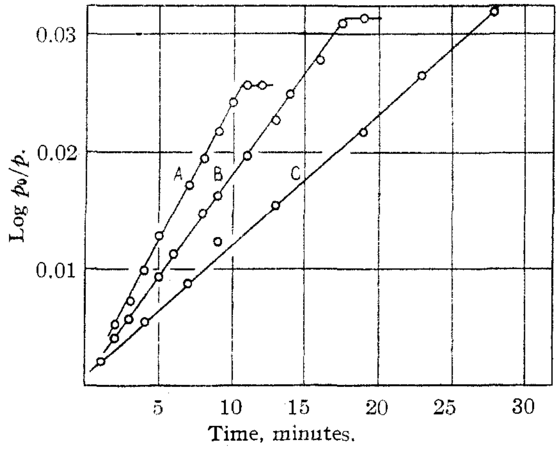

Fig. 1.—Plots for hydrogenation of the cyclohexadienes and benzene: A, 1,3-cyclohexadiene; B, 1,4-cyclohexadiene; C, benzene.

TABLE I

EFFECT OF VARIABLES ON THE RATE OF HYDROGENATION

| Hydrocarbon | Ml. | Grams of catalyst | Initial pressure, (p. s. i.) | $k° \times 10^3$ (liters/g. min.) |
|---|---|---|---|---|
| Cyclohexene | 5 | 0.02 | 64.2 | 2260 |
| Cyclohexene | 5 | .02 | 28.0 | 2395 |
| Cyclohexene | 5 | .005 | 64.3 | 2170 |
| Cyclohexene | 10 | .005 | 64.0 | 2260 |
| Cyclohexadiene-1,3 | 5 | .02 | 64.6 | 1840 |
| Cyclohexadiene-1,3 | 2.5 | .02 | 29.6 | 1983 |
| Cyclohexadiene-1,3 | 5 | .01 | 64.2 | 1640 |
| Cyclohexadiene-1,3 | 2.5 | .02 | 64.1 | 1995 |
| Cyclohexadiene-1,4 | 6 | .02 | 64.0 | 1240 |
| Cyclohexadiene-1,4 | 2.5 | .02 | 30.0 | 1330 |
| Cyclohexadiene-1,4 | 5.0 | .01 | 64.2 | 1110 |
| Cyclohexadiene-1,4 | 2.5 | .02 | 64.3 | 1165 |

TABLE II

RATE CONSTANTS AND ACTIVATION ENERGIES

| Hydrocarbon | $k^\circ_{30} \times 10^3$ (liters/g. min.) | Activation energy (cal./mole) |
|---|---|---|
| Cyclohexene | 2350 | 2400 |
| Cyclohexadiene-1,3 | 1900 | 4500 |
| Cyclohexadiene-1,4 | 1330 | 4000 |
| Benzene | 290 | 7400 |

Figure 1 shows typical plots for the calculation of rate constants, and Fig. 2 shows the graphs from which the activation energies were calculated. It is estimated that the error in these values is of the order of ±300 calories.

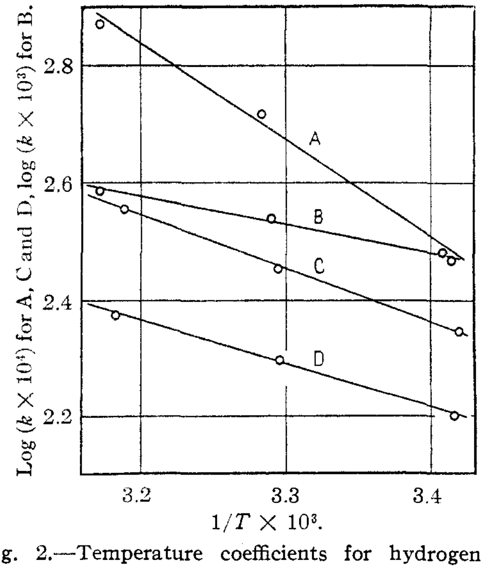

Fig. 2.—Temperature coefficients for hydrogenation reactions: A, benzene; B, cyclohexene; C, 1,3-cyclohexadiene; D, 1,4-cyclohexadiene.

## Discussion

Since these hydrogenations are all zero order with respect to the hydrogen acceptor, it follows that differences in the heats of adsorption of the cyclohexene, cyclohexadienes, and benzene on

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[2] Kistiakowsky, Ruhoff, Smith and Vaughan, THIS JOURNAL, **58**, 146 (1936).

[3] M. P. Doss, "Physical Constants of the Principal Hydrocarbons," Technical and Research Division of the Texas Co., New York, N. Y., 1944, p. 159.

[4] Adams, Voorhees and Shriner, "Organic Syntheses," **8**, 92 (1928).

[5] Smith, Alderman and Nadig, THIS JOURNAL, **67**, 272 (1945).

[6] Fuzek and Smith, *ibid.*, **70**, 3743 (1948).

platinum cannot be involved in the activation energies. Since all other factors remain constant, the differences in the apparent activation energies for the catalytic reactions must represent differences in the true activation energies for the hydrogenation of these compounds on platinum.

The heats of hydrogenation of cyclohexene, 1,3-cyclohexadiene, and benzene are −28,600, −55,400, and −49,800 cal. respectively.[2,7] The corresponding value for 1,4-cyclohexadiene may be estimated as twice that of cyclohexene, or −57,200. If one assumes that the hydrogenation of benzene proceeds by the path benzene → 1,3-cyclohexadiene → cyclohexene → cyclohexane, and that the first step is rate determining, it is necessary that the energy of activation for the hydrogenation of benzene, catalytically or otherwise, be at least 5600 calories. If, by any possibility, the hydrogenation of benzene should pass through the intermediate 1,4-cyclohexadiene, the energy of activation would have to be at least 7,400 calories. The actual energy of activation, 7,400 cal., is surprisingly close to either of these requirements.

The resonance stabilization of the benzene ring as calculated from the heats of hydrogenation is 36,000 calories.[2] One would probably expect the activation energy for the hydrogenation of benzene to be at least equal to this value. If this reasoning is correct, it would appear that the benzene molecule must be adsorbed on the platinum catalyst in such a manner that its resonance is destroyed, and that the slow rate of hydrogenation of the benzene nucleus when compared to that of simple unsaturated compounds cannot be attributed to resonance.

It is also interesting to note that the conjugated 1,3-cyclohexadiene has a faster rate of hydrogenation than is found for the unconjugated 1,4-cyclohexadiene. The difference in the activation energies is probably within experimental error.

## Summary

The catalytic hydrogenations of benzene, the cyclohexadienes, and cyclohexene on platinum have been studied from a kinetic viewpoint. Rate constants and activation energies have been determined for each of these reactions. The low value for the activation energy of the hydrogenation of benzene when compared with the resonance energy of the molecule indicates the probability that such resonance is destroyed when the benzene is adsorbed on the catalyst.

KNOXVILLE, TENNESSEE RECEIVED AUGUST 20, 1948

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[7] Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **58**, 137 (1936).

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[CONTRIBUTION NO. 60 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF TENNESSEE]

# Catalytic Hydrogenation of Furan and Substituted Furans on Platinum

BY HILTON A. SMITH AND JOHN F. FUZEK

Studies of the kinetics of catalytic hydrogenation of the benzene nucleus on Adams platinum catalyst have been previously reported.[1,2] This work has now been extended to include furan and several substituted furan compounds. The aim has been to determine in a quantitative manner the effect of structure on the rate of hydrogenation of the furan nucleus with Adams platinum catalyst in acetic acid solution. Particular attention has been given the effect of varying the type of the substituent group on the rate. The results obtained have been compared with those for corresponding benzene compounds. Where necessary for such comparisons, additional work was also done in the benzene series.

## Experimental

**Preparation of Materials.**—**Furan** and **2-methylfuran** (E. I. du Pont de Nemours and Company) were treated with Raney nickel catalyst, dried, and fractionated in a ten-foot Vigreux column.

**Furoic acid** (Eastman Kodak Company) was purified by recrystallization and subsequent conversion to the methyl ester. This was dried, treated with Raney nickel and activated charcoal, and fractionated. The product (b. p. 181.8–182.0 (736 mm.), $n^{20}\mathrm{D}$ 1.3880) was converted to the acid which was recrystallized and dried.

**2,5-Dimethylfuran** (Eastman Kodak Company) was azeotropically distilled with methanol (azeotrope b. p. 60.8° (743 mm.), 35–40% by volume 2,5-dimethylfuran), separated after addition of water, dried and fractionated.

**Benzyl alcohol** and **benzoic acid** were Eastman products. The alcohol was treated with Raney nickel and anhydrous magnesium sulfate, and fractionated. As in previous work, the benzoic acid was used without further purification.

**Furfural** and **furfuryl alcohol** (Quaker Oats Company) were treated with Raney nickel catalyst, anhydrous magnesium sulfate and activated charcoal for several hours. The solids were removed by filtration and the furan derivatives distilled through a fourteen-foot Vigreux column. The center fractions boiled within a 0.1° range.

**Dibenzofuran** (diphenylene oxide) (The Reilly Tar and Chemical Corporation) was treated with Raney nickel catalyst and activated charcoal in hot ethanol solution. The solution was filtered several times and the crystals recovered on cooling. They were then recrystallized from benzene. This cycle was repeated three times. The resulting crystals when dry melted within a range of 0.5°. Further purification failed to narrow this melting range.

The **Adams platinum catalyst** was prepared from 3.5-g. batches of platinum chloride in the usual manner.[3] Several of these finished batches of catalyst were mixed and then standard rates obtained as in previous work.[1] The acetic

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[1] Smith, Alderman and Nadig, THIS JOURNAL, **67**, 272 (1945).

[2] Smith and Pennekamp, *ibid.*, **67**, 276 (1945).

[3] Adams, Voorhees and Shriner, "Organic Syntheses," **8**, 92 (1928).