m.p. or b.p. agreed with the literature values. For the other materials see Part I.

**General Procedure.**—A solution of 0.002 mole of sulfanilic acid and of 0.002 mole of a substituted aniline in 80 cc. of 0.625 $N$ sulfuric acid was placed into a 200-cc. erlenmeyer flask and cooled to 0°. In another flask 20 cc. of 0.1 $N$ sodium nitrite solution was cooled to 0°. The solutions were mixed, allowed to stand for 2 hours and run into an alkaline solution of β-naphthol as described in Part I. The coupling product of the diazotized sulfanilic acid (Orange II) remains in solution and the azo compound formed from the substituted aniline studied is collected and estimated as in Part I.

**Experimental Results and Calculations.**—The following rate equations apply to the case of competitive diazotization of a substituted aniline B in the presence of sulfanilic acid A

$$\left\{\begin{aligned} \mathrm{d}x_A/\mathrm{d}t &= (k_A/K_A)(a - x_A)(b - x_A - x_B)^2 \\ \mathrm{d}x_B/\mathrm{d}t &= (k_B/K_B)(a - x_B)(b - x_A - x_B)^2 \end{aligned}\right. \qquad (13)$$

where $K_A$ and $K_B$ are equilibrium constants in equation 5, $k_A$ and $k_B$ are rate constants, and $x_A$ and $x_B$ are the diazonium salt concentrations at time $t$. Thus $k_B$ may be expressed as a function of the other five variables.

$$\frac{\mathrm{d}x_A}{a - x_A} = \frac{k_A K_B}{k_B K_A}\frac{\mathrm{d}x_B}{a - x_B}$$

$$k_B = K_B \left\{\frac{\log(1 - (x_B/a))}{\log(1 - (x_A/a))}\right\} \frac{k_A}{K_A} \qquad (14)$$

Since $K_A$, $K_B$ and $x_B$ are known or measurable, and since upon complete consumption of nitrous acid the sum $(x_A + x_B)$ equals the total amount of nitrite added, $k_B$ may be computed. Table III lists the results, where $x_B/a$ and $x_A/a$ represent the fractions diazotized of the two competing amines. From the rate relative to aniline the ρ-factor for Hammett's equation[12] was calculated as shown in the Table III.

TABLE III

RELATIVE RATES OF DIAZOTIZATION OF SUBSTITUTED ANILINES AT 0°

Initial concentration: 0.02 $M$ for aniline and for sulfanilic acid; 0.5 $N$ for sulfuric acid; 0.02 $N$ for nitrous acid; $p$H 0.6; reaction time 2 hours

| Substituent | $x_B/a$ | $x_A/a$ | $K_B \times 10^{-6}$ [a] | Relative rate: Based on sulfanilic acid,[b] | Relative rate: Based on aniline | ρ |
|---|---|---|---|---|---|---|
| $m$-$CH_3$ | 0.264 | 0.736 | 2.71 | 0.62 | 1.38 | −2.12 |
| $p$-$CH_3$ | .209 | .791 | 6.5 | 0.98 | 2.18 | −1.99 |
| $p$-$OCH_3$ | .192 | .808 | 10.8 | 1.39 | 3.10 | −1.94 |
| $p$-$OC_2H_5$ | .223 | .777 | 9.8 | 1.65 | 3.67 | −2.26 |
| None | .255 | .745 | 2.10 | 0.450 | 1.00 | .... |
| $m$-Cl[c] | .421 | .579 | 0.158 | .100 | 0.222 | −1.75 |
| $p$-Cl | .340 | .660 | .47 | .183 | .407 | −1.72 |
| $m$-$NO_2$[c] | .518 | .482 | .022 | .024 | .053 | −1.80 |
| $p$-$NO_2$[c] | .867 | .133 | .0055 | .0011 | .0022 | −2.08 |
| | | | | | Av. | −1.96 ± 0.05[d] |

[a] H. Landolt–R. Börnstein, "Physikalischen Chemische Tabellen," Eg. II, Eg. III, 5 Aufl., Julius Springer, Berlin, 1936. Calculated from the basicity constant $K$ at 25°; $K_B = K[H_2O]/K_w = K \times 55 \times 10^{14}$. [b] Since the value of $K_A$ was unavailable, these values were shown in $(K_A/10^6)$ unit, *e.g.*, the relative rate of $m$-toluidine is $0.62 \times 10^{-6}/K_A$. [c] Became a little turbid during the reaction. [d] Probable error.

Apparently electron-releasing groups in the $p$-position facilitate the electrophilic attack by $HN_2O_3^+$ while with electron-withdrawing groups the reverse is true. The effect of substituents on the rate of the reaction may be expressed by a Hammett equation with an average ρ-value of −1.96 ± 0.05.

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KYOTO, JAPAN

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[12] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 186.

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[CONTRIBUTION FROM THE MULTIPLE FELLOWSHIP OF GULF RESEARCH AND DEVELOPMENT COMPANY, MELLON INSTITUTE]

# Fischer–Tropsch Synthesis Mechanism Studies. The Addition of Radioactive Alcohols to the Synthesis Gas

BY J. T. KUMMER AND P. H. EMMETT

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When one of the radioactive primary alcohols, such as ethanol, $n$-propanol or isobutyl alcohol, is added to the extent of about 1.5 volume per cent. to a 1:1 hydrogen:carbon monoxide synthesis gas and passed over an iron catalyst at 235° and one atmosphere pressure, the hydrocarbon synthesis products in the $C_2$–$C_{10}$, $C_3$–$C_{10}$ and $C_4$–$C_{10}$ ranges, respectively, are found to have an approximately constant molal radioactivity equal to one-third to one-half the molal radioactivity of the original alcohol. These results show that primary alcohols adsorbed on iron catalysts can act as starting nuclei in building up higher hydrocarbons. Adsorbed methanol can also start reaction chains leading to higher hydrocarbons, but the efficiency of incorporation is only about one-fourth as great as with the other primary alcohols mentioned above. Isopropyl alcohol, a secondary alcohol, is extensively converted to isobutane and isobutene but only about one $C_7$ molecule in 15 and one $C_9$ molecule in 27 comes from the isopropyl alcohol. $t$-Butyl alcohol is apparently not capable of building up to higher hydrocarbons under the conditions of these experiments. In the runs in which radioactive normal propanol was added to the synthesis gas the $n$-$C_4H_{10}$ formed was radioactive; the $i$-$C_4H_{10}$, non-radioactive. Conversely, when radioactive isopropyl alcohol was added, the $n$-$C_4H_{10}$ was non-radioactive; the $i$-$C_4H_{10}$, radioactive. The results are interpreted as indicating that complexes resembling adsorbed alcohols are formed from carbon monoxide and hydrogen during synthesis and act as intermediates in the building up of higher hydrocarbons over iron catalysts.

When a small amount of radioactive ethanol is added to a 1:1 carbon monoxide–hydrogen synthesis gas mixture and passed over an iron catalyst at about 235°, the $C_2$ to $C_{10}$ hydrocarbon synthesis product has been shown[1] to have an approximately constant radioactivity per mole. This has been interpreted as indicating that the complex formed by the adsorption of ethanol on the iron catalyst is capable of acting as an intermediate in the synthesis of higher hydrocarbons. Pyrolysis of the propane from these experiments showed, furthermore, that carbon atoms attach themselves preferentially

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[1] J. T. Kummer, W. B. Spencer, H. H. Podgurski and P. H. Emmett, THIS JOURNAL, **73**, 564 (1951).

to the 1-carbon of the alcohol complex. The experiments described in the present paper represent an extension of this technique and involve the use of radioactive methanol, *n*-propanol, isopropyl alcohol, and isobutyl alcohol, and of non-radioactive *t*-butyl alcohol. The hydrocarbon products in each of the runs with radioactive alcohols have been examined to see whether their radioactivity is consistent with the hypothesis that the molecules of each of the alcohols act as starting nuclei for building up hydrocarbon molecules by chain growth and to see whether growth takes place exclusively at the 1-carbon atom.

## Experimental

The same one atmosphere, fixed bed, Fischer–Tropsch synthesis unit was used as described in the earlier paper,[1] with the addition of a Dry Ice trap between the ice trap and the soda lime tube. The liquid product, including the liquid which is caught in a trap at −195°, was washed with water and distilled from sodium hydride to ensure removal of any of the original alcohol that may have been present. The remaining liquid was fractionated into cuts of different molecular weight by a one-plate, low temperature (−80 to −30°) distillation in high vacuum.[2] These cuts were burned to carbon dioxide and counted as described in the previous paper.

The gaseous products were separated into $C_1$, $C_2$, $C_3$ and $C_4$ fractions by distillation in a Podbielniak column. In addition, in a few runs, the isobutane, *n*-butane, isobutene and *n*-butene were separated from each other and analyzed for their specific radioactivities. In the isopropyl alcohol run, after the olefins were removed by absorption, the *n*-butane and isobutane were separated by means of a small adsorption fractionator similar to that described by Turner[3]; in the first normal propanol run, the separation of $n$-$C_4H_{10}$ and $i$-$C_4H_{10}$ was effected by means of dehydrated chabazite[4] as suggested by Barrer.[5] The olefins in the $C_4$ fraction were, of course, removed by absorption prior to the chabazite separation and to the radioactive analysis of the isobutane and *n*-butane. In the experiments with *n*-propanol, the specific radioactivities of the olefins were determined by subjecting the butene–butane mixture to hydrogenation over an iron synthetic ammonia catalyst at room temperature until substantially all of the olefin content was hydrogenated. A chabazite separation and a radioactive count of the resulting isobutane, and *n*-butane, together with a suitable correction for the isobutane and *n*-butane originally present, then gave specific activities for the portion of the gas that was present originally either as isobutene or *n*-butene.

In all cases the separated $C_1$ to $C_4$ gases used for radioactive tests were analyzed by means of a mass spectrometer. The amount of alcohol present in the aqueous layers of the ice and Dry Ice traps was determined by distillation.

Two iron synthetic ammonia catalysts were used for synthesis. Number 333 contained, before reduction, 2.82% $Al_2O_3$ and 1.39% $ThO_2$ in addition to $Fe_3O_4$; number 955 contained 7.95% $Al_2O_3$ in addition to $Fe_3O_4$.

The radioactive methanol was purchased from Tracerlab, Incorporated. The isopropyl alcohol was prepared from radioactive methyl iodide purchased from Tracerlab, Incorporated. The iodide was converted to the Grignard reagent which was then permitted to react with acetaldehyde to give the radioactive isopropyl alcohol. The *n*-propanol in the first *n*-propanol run was prepared by reduction of propionic acid by lithium aluminum hydride. A small amount of radioactive sodium 2-$C^{14}$-propionate received from the University of California was dissolved in 20 cc. of propionic acid which was then reduced. The alcohol used in the second *n*-propanol run was prepared in this same way from carboxy-labeled sodium propionate purchased from the Texas Research Foundation. The radioactive isobutyl alcohol was prepared from the radioactive isopropyl alcohol made as above. The isopropyl alcohol was converted to the bromide by $PBr_3$, then to the Grignard reagent and then to the isobutyl alcohol by reaction with formaldehyde gas. The alcohol–water constant boiling mixtures were dehydrated with calcium carbide and the resultant anhydrous alcohols purified by distillation. The alcohols were introduced into the inlet gas stream by bubbling the gas through the liquid alcohol held at appropriate temperatures.

## Results

Table I summarizes the experimental conditions and the amount of product formed in the various Fischer–Tropsch synthesis runs. Table II gives the radioactivity of hydrocarbon products as a function of the number of carbon atoms in each molecule. The values of the radioactivities are given to three places in Table II though the over-all accuracy of such figures is probably no better than ±5%.

TABLE I

DATA FOR FISCHER–TROPSCH SYNTHESIS RUNS OVER AN IRON CATALYST WITH 1:1 $H_2$ TO CO SYNTHESIS GAS AT ONE ATMOSPHERE PRESSURE

| Radioactive alcohol added | Methanol run | *n*-Propanol run No. 1 | *n*-Propanol run No. 2 | Isopropyl alcohol run | Isobutyl alcohol run |
|---|---|---|---|---|---|
| Catalyst used, no. | 955 | 333 | 955 | 333 | 333 |
| Catalyst, vol., cc. | 50 | 45 | 50 | 45 | 45 |
| Space velocity, 1/hr. | 240 | 270 | 240 | 270 | 270 |
| Temp. of bed, °C. | 222 | 243 | 229 | 228 | 226 |
| Duration in hr. | 34.6 | 23.5 | 34.2 | 21 | 24 |
| Alcohol introduced, g. | 11.2 | 11.0 | 17.7 | 10.2 | 11.5 |
| Alcohol in inlet gas, vol. % | 1.9 | 1.5 | 1.6 | 1.5 | 1.2 |
| Contraction, vol. % after liq. $N_2$ trap | 16 | 14 | 12 | 16 | 12 |
| $CO_2$ produced in g. | 21.4 | <13 | 15.6 | .... | 10 |
| Water produced in g. | 10.3 | | 7.4 | .... | .... |
| Alcohol in ice + Dry Ice trap, g. | 5.6 | 5.9 | 7.4 | >2.9 | .... |
| Oil hydrocarbons, g. | 1.4 | 1 | 1.4 | 2 | 2 |
| Gasol hydrocarbons, g. | 2.4 | 1.4 | 0.9 | | |
| Gaseous hydrocarbon, cc. (S.T.P.) | 2400 | 1000 | 2000 | 4000 | 2000 |
| Analysis of gas fraction, vol. % | | | | | |
| Methane | 9.6 | ....[a] | 3.0 | 2.5 | 3.2 |
| Ethane | 22.4 | .... | 10.4 | 11.3 | 10.4 |
| Ethylene | 17.0 | .... | 19.8 | 12.5 | 26.5 |
| Propane | 6.9 | .... | 5.6 | 15.9 | 3.3 |
| Propylene | 27.4 | .... | 35.5 | 41.6 | 29.1 |
| Butanes | 2.4 | .... | 2.8 | 2.3 | 3.9 |
| Butenes | 10.8 | .... | 17.6 | 9.9 | 18.3 |
| $C_5$ | 3.5 | .... | 5.3 | 4.0 | 5.3 |
| % Olefins | 55 | .... | 73 | 64 | 74 |

[a] Complete distillation analysis of the product of this run was not made. However, a mass spectrographic analysis of the $C_2$ cut showed $C_2H_4:C_2H_6 = 7.52:1$; that of a $C_3$ cut showed $C_3H_6:C_3H_8 = 11.7:1$; and that of a $C_4$ cut freed of $C_3$ and $C_5$ showed 6% $n$-$C_4H_{10}$, 0.4% $i$-$C_4H_{10}$, 5.4% isobutylene, 88.2% butene-1, and 0% butene-2.

An exact balance of the inlet and exit radioactive carbon was not essential in the present work. Nevertheless a partial summary of the amount of $C^{14}$ in the exit gases is given in Table III. Some of the missing $C^{14}$ was probably retained by the catalyst as wax; additional amounts may have been converted into iron carbide or carbon.

Before attempting to draw conclusions as to the significance of the present experimental results taken as a whole, it will be desirable to discuss the details and implications of the individual experiments.

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[2] D. J. LeRoy, *Can. J. Research*, **B28**, 492 (1950).

[3] N. C. Turner, *Petroleum Refiner*, **22**, No. 5, 140 (1943).

[4] The two-gram chabazite sample used in these separations was ground to 200 mesh and then dehydrated for 16 hours at 300° and 3 hours at 475°. Adsorption was sufficiently complete in about one hour's exposure of the hydrocarbon sample to the chabazite at 100°.

[5] R. M. Barrer, *Trans. Faraday Soc.*, **40**, 195 (1944).

TABLE II

RADIOACTIVITY OF THE PRODUCTS AND ORIGINAL ALCOHOL OF THE SYNTHESIS RUNS (COUNTS PER MINUTE PER CC. (S.T.P.))

| Substance | Methanol run Carbon no. | Methanol run Activity | *n*-Prop.,[a] run 1 Carbon no. | *n*-Prop.,[a] run 1 Activity | *n*-Prop.,[b] run 2 Carbon no. | *n*-Prop.,[b] run 2 Activity | Isoprop.,[c] run Carbon no. | Isoprop.,[c] run Activity | Isobut.,[d] run Carbon no. | Isobut.,[d] run Activity |
|---|---|---|---|---|---|---|---|---|---|---|
| Original radioactive alcohol | 1 | 5000 | 3 | 6780 | 3 | 5630 | 3 | 6850 | 4 | 2400 |
| CO | 1 | 32 | 1 | ... | 1 | 5 | 1 | .. | 1 | .. |
| $CO_2$ | 1 | 175 | 1 | .. | 1 | .. | 1 | .. | 1 | .. |
| Methane | 1 | 360 | 1 | 0 | 1 | 45 | 1 | 30 | 1 | .. |
| Ethane | 2 | 480 | 2 | 158 | 2 | 74 | 2 | 20 | 2 | 0 |
| Ethylene | 2 | 310 | 2 | 95 | 2 | 47 | 2 | 20 | 2 | 0 |
| $C_2$ as a whole | 2 | 400 | 2 | 103 | 2 | 56 | 2 | 20 | 2 | 0 |
| Propane | 3 | 740 | 3 | 5000 | 3 | 3550 | 3 | 4770 | 3 | 150 |
| Propylene | 3 | 430 | 3 | 2510 | 3 | 2150 | 3 | 3640 | 2 | 49 |
| $C_3$ as a whole | 3 | 500 | 3 | 2710 | 3 | 2340 | 3 | 3950 | 3 | 59 |
| Butanes | 4 | 730 | 4 | 2470 | 4 | 3070 | 4 | 340 | 4 | 1430 |
| *n*-Butane | 4 | .. | 4 | 2630 | 4 | 3100 | 4 | 30 | 4 | .. |
| Isobutane | 4 | .. | 4 | 0 | 4 | .. | 4 | 4370 | 4 | .. |
| Butenes | 4 | 510 | 4 | 2380 | 4 | 3290 | 4 | 1070 | 4 | 690 |
| *n*-Butenes | 4 | .. | 4 | 2500[e] | 4 | .. | 4 | 300 ± 100 | 4 | .. |
| Isobutene | 4 | .. | 4 | <450 | 4 | 1050 | 4 | 4200 ± 300 | 4 | .. |
| $C_4$ as a whole | 4 | 550 | 4 | 2460 | 4 | 3270 | 4 | 900 | 4 | 820 |
| Liquid | 5 | 600 | 5.1 | 2680 | 5.3 | 3250 | 6.8 | 440 | 6.0 | 870 |
|  | 5 | 636 | 5.5 | 2820 | 6.0 | 3160 | 7.1 | 390 | 6.1 | 800 |
|  | 5.8 | 710 | 6.2 | 2550 | 7.0 | 3020 | 7.7 | 330 | 6.1 | 1180 |
|  | 6.7 | 785 | 6.6 | 2740 | 8.2 | 3140 | 7.8 | 300 | 6.3 | 590 |
|  | 8.1 | 855 | 6.8 | 2770 | 10.6 | 3340 | 8.0 | 260 | 6.3 | 980 |
|  | 8.8 | 860 | 7.0 | 2740 | .. | .. | 8.9 | 250 | 6.4 | 920 |
|  | 11.0 | 1010 | 7.1 | 2780 | .. | .. | ... | .. | 7.0 | 960 |
|  | .. | .. | 7.2 | 2820 | .. | .. | ... | .. | 9.5 | 530 |
|  | .. | .. | 7.7 | 3420 | .. | .. | ... | .. | ... | .. |
|  | .. | .. | 7.8 | 3810 | .. | .. | ... | .. | ... | .. |
|  | . | .. | 8.1 | 4590 | .. | .. | ... | .. | ... | .. |

[a] *n*-Propanol-2$C^{14}$ ($CH_3C^{14}H_2CH_2OH$). [b] *n*-Propanol-1$C^{14}$ ($CH_3CH_2C^{14}H_2OH$). [c] Methyl labeled isopropyl alcohol ($C^{14}H_3CHOHCH_3$). [d] Methyl labeled isobutyl alcohol $\genfrac{}{}{0pt}{}{C^{14}H_3}{CH_3}\!>\!CH_1CH_2OH$. [e] In this run the *n*-butene sample was shown to be entirely butene-1; the activity of the number one carbon atom was zero.

TABLE III

RADIOACTIVITY MATERIAL BALANCE EXPRESSED AS PER CENT.[a] OF THE RADIOACTIVITY OF THE ORIGINAL ALCOHOL

| Product | Methyl alcohol run | *n*-Propanol run 1 | *n*-Propanol run 2 | Isopropyl alcohol run | Isobutyl alcohol run |
|---|---|---|---|---|---|
| Aqueous product | 50 | ... | 42 | >28 | ... |
| CO off gas | 17 | ... | 2.7 | ... | ... |
| Gaseous hydrocarbon products | 2.8 | ~6 | 9.8 | 36.5 | 6 |
| Liquid hydrocarbon products | ~1 | ~5 | ~3 | ~0.3 | ~4 |
| $CO_2$ | 4.9 | ... | ... | ... | ... |

[a] No attempt was made to account for all of the radioactivity of the inlet alcohol. Probably some of the radioactive carbon remained in the catalyst as carbide or as high molecular weight wax.

**Methanol Run.**—The radioactivity appearing in the carbon monoxide in this run may have come from partial decomposition of the methanol. The volume per cent. of methanol (1.5%) used is several times higher than the per cent. of methanol in equilibrium with a 1:1 hydrogen–carbon monoxide mixture at one atmosphere and 222°. The presence of high activity (175 counts per minute per cc.) in the carbon dioxide of this run is difficult to explain when one makes the usual assumption that the carbon dioxide is produced from CO and $H_2O$ by the water–gas shift reaction. If all of the radioactive carbon corresponding to the observed exit concentrations of carbon monoxide, carbon dioxide and hydrocarbon had appeared at the entrance of the catalyst bed as radioactive carbon monoxide, the total activity in counts per minute per cc. of the carbon monoxide would have been raised to only 47. This is too low to account for the observed value of 175 for the carbon dioxide. Apparently, at least part of the carbon dioxide is due to some side reaction involving the radioactive methanol.

The hydrocarbon activity when plotted against the carbon number, gives an approximate straight line of a slope of 70 counts per minute per cc. of hydrocarbon for each unit increase in carbon number. It corresponds to an ordinate of 350 counts per minute per cc. at a carbon number of one. The amount by which the slope of this line (70 counts per cc. per added carbon atom) exceeds the activity of the carbon monoxide (32 counts per minute per cc.) can be taken as evidence that there is a tendency for the complex resulting from adsorbed methanol to enter the chain-building and not just the chain-initiating step.

For 1.5% methanol in the synthesis gas, over singly promoted catalyst 955, only about one hydrocarbon molecule in twelve appears to originate from a complex formed by the adsorption of methanol on the catalyst surface. This is to be compared with values of one hydrocarbon molecule in every two or three during a synthesis run being formed from the addition of about 1.5% of ethyl, *n*-propyl or isobutyl alcohol.

The per cent. olefin in the methanol run was the same as in the control runs made just before and just after the methanol run. This behavior is different from that observed in the ethanol, propanol and butanol runs, in which the introduction of the alcohol caused an increase in olefin production. (This latter behavior is discussed in reference 1.) Apparently, the higher alcohols poison the catalyst much more than methanol for the hydrogenation of olefins to paraffins during a run. This may mean that water vapor produced from the alcohols is the real hydrogenation poison and that the poisoning action of methanol is less serious because it cannot produce a hydrocarbon and water by dehydration.

***n*-Propanol Runs.**—The participation of *n*-propanol in the reaction is very similar to that of ethanol. In the first propanol run, the activity of the high molecular weight liquid samples increased suddenly at the carbon number of eight. It was suspected that this increase was caused by the polymerization of the small amount of olefinic $C_4$ hydrocarbons that were present in the original liquid. This seemed especially likely because this liquid sample, unlike any other, was allowed to stand over sodium metal for several weeks after drying. To check this cause of the difficulty, a second *n*-propanol run was made. In it the liquid product was not treated any further after distillation from the sodium hydride. In this second run, the increase in activity in the $C_8$–$C_{10}$ range was not observed.[6]

About one product molecule in two in the second *n*-propanol run originated from an alcohol molecule. The existence of a finite though small activity of the $C_1$ and $C_2$ fractions may indicate a small amount of cracking of the *n*-propanol. Evidence of this can be seen by comparing the activity of the $C_1$–$C_2$ fraction in the run using 2-labeled *n*-propanol with this same fraction in the run using 1-labeled *n*-propanol. If a small amount of the 2-labeled propanol (or propane) cracked to ethane and methane, one would expect that the radioactive carbon would show up in the $C_2$ fragment and not in the $C_1$ fragment. This agrees with the zero activity for methane and the 103 activity for the $C_2$ fraction shown in Table II. On the other hand, in the run using 1-labeled propanol, the radioactivity of the $C_1$ and $C_2$ fractions should be approximately equal. This prediction, too, is borne out by the values (Table II) of 45 and 56 for the activities of the $C_1$ and $C_2$ fractions in the second *n*-propanol run.

The activity of the isobutane from the first *n*-propanol run is zero compared to a value of 2630 for the *n*-butane. The isobutene activity seems to be less than 25% of the activity of the *n*-butene in the first *n*-propanol run and about 30% in the second. In view of the zero value obtained for isobutane in the first *n*-propanol run, it seems very likely that the isobutene was contaminated with radioactive isobutene formed by partial skeletal isomerization of radioactive *n*-butene during the catalytic hydrogenation at room temperature over an iron catalyst, and that the added *n*-propanol really gave rise to *n*-$C_4$ but not to iso-$C_4$ hydrocarbons.

It is also interesting to note that the $C_4$ fraction from the first *n*-propanol run contained no butene-2 thus indicating the absence of any double bond shifting in the olefins during synthesis in contrast to the shift observed in the double bond of propylene in the ethyl alcohol run.[1] Furthermore, the activity of the 1-carbon atom of butene-1 was zero. This latter result is to be expected in the absence of skeletal isomerization during the synthesis run since the original *n*-propanol was labeled in the 2-position.

**Isopropyl Alcohol Run.**—The high activity of the isobutane (4370) and the low activity of the *n*-butane (30) in the products of this run indicate that carbon addition takes place almost exclusively on the middle carbon of the isopropyl alcohol. This is also borne out by the figures given in Table II for the isobutene (4200 ± 300) and the *n*-butene (300 ± 100), though unfortunately the analysis of the $C_4$ olefins for radioactivity in this run is somewhat less dependable than the analysis of the saturated portion of the $C_4$ fraction. The $C_4$ cut contained about 72% *n*-butene and 12.5% isobutene. Because the boiling points of these butenes are so close together, the charcoal column[3] used in this run could not separate the two sufficiently well to permit the activity of the *n*-butene and isobutene to be fixed with great accuracy. However, even the approximate figures of 300 and 4200 for the activities of the normal butene and isobutene, respectively, enable us to conclude that the normal butene is probably less than 10% as active as the isobutene and that, accordingly, both the olefins and the paraffins in the $C_4$ cut indicate that the carbon adds almost exclusively to the middle carbon atom of the isopropyl alcohol.

It is apparent from the data in Table II that this secondary alcohol did not enter into the building of higher hydrocarbons to the same extent as the primary alcohols, ethanol, propanol and isobutyl alcohol. Only one molecule in seven of the $C_4$ hydrocarbons and one in twenty-seven of the $C_9$ hydrocarbons were produced from the radioactive isopropanol. This low efficiency of incorporation into the $C_4$ and higher hydrocarbons is apparently to be attributed to the tendency pointed out above for isopropyl alcohol to form iso-$C_4$ rather than *n*-$C_4$ products. Since experience[7] has shown that nine times as much *n*-$C_4$ hydrocarbons are formed as *i*-$C_4$ hydrocarbons in regular synthesis, it follows that even if a large fraction of the isobutane and isobutene came from the radioactive isopropyl alcohol, the over-all percentage of radioactive hydrocarbons in the $C_4$ fraction as a whole would be relatively small. In this connection it should, however, be pointed out that the reason is not known for the steady drop in the radioactivity of the hydrocarbon

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[6] An alternate explanation of the sudden rise in activity at a distillation point corresponding to about the $C_8$ hydrocarbon fraction in the first *n*-propanol run, was the possible formation of some *n*-propyl ether during the run. However, an infrared analysis failed to detect any of this compound in the products.

[7] (a) F. H. Bruner, *Ind. Eng. Chem.*, **41**, 2511 (1949); (b) A. W. Weitkamp, H. S. Seelig, N. J. Bowman and W. E. Cady (to be published).

fractions from 900 for the $C_4$ hydrocarbons to 250 for $C_9$ hydrocarbons.

The high activity of the $C_3$ fraction in the isopropyl alcohol run is of interest for several reasons. In the first place it suggests relatively strong adsorption of the isopropyl alcohol on the catalyst surface and thus indicates that the failure of the isopropyl alcohol to build into the higher hydrocarbons is probably not the lack of adsorption of the isopropyl alcohol to form an adsorbed complex on the catalyst surface.[8] The second and perhaps more significant conclusion to be drawn from the high activity of the $C_3$ fraction has to do with the propylene. The activity and the amount of this $C_3$ olefin is considerably higher in the run with isopropyl alcohol than in those with normal propyl alcohol. In spite of this, the radioactivity of the higher hydrocarbons is very much less in the runs containing radioactive isopropyl alcohol than in the runs containing radioactive *n*-propanol. This seems to constitute definite confirmation of our belief that the olefin itself[9] is not the primary intermediate responsible for the incorporation of the radioactivity of the normal primary alcohols into the higher hydrocarbons.

The propane from this isopropyl alcohol run was thermally cracked at 575°. The methane produced had one-half the activity of the propane. This is to be expected if no skeletal isotopic isomerization of the propane took place during the synthesis run. The small but equal activity in the $C_1$ and $C_2$ fractions in the run using radioactive isopropanol would be expected to result from a small amount of cracking of the methyl-labeled isopropyl alcohol or propane.

**Isobutyl Alcohol Run.**—This primary alcohol appears to behave like ethanol in being able to serve as a starting nucleus in building up higher hydrocarbons. About one molecule in three of the liquid product originates from an alcohol molecule. The erratic activity obtained for the liquid fraction may be due to partial separation of isomers in the distillation, since the radioactive molecules of the liquid hydrocarbons would all contain the isobutyl structure as part of the molecule. The zero activity of the $C_2$ fraction indicates that any cracking of the radioactive isobutyl alcohol (or of the isobutane or isobutene formed from the alcohol) that takes place does not involve the formation of a $C_2$ group containing one of the methyl groups of the original alcohol.

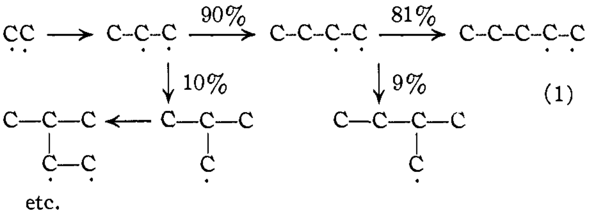
One further comment should be made on this isobutyl alcohol run. The single experimental point for a $C_{9.5}$ hydrocarbon has a low value of 550 compared to a value of 820 for the $C_4$ fraction and an average value of 890 for the $C_6$–$C_7$ fraction. There is accordingly some uncertainty in this run as to whether the radioactivity per mole of hydrocarbon remains constant over the $C_7$–$C_{9.5}$ range or drops slowly as the carbon number increases above seven. Additional work will be necessary to clear up this point though the constancy of the activity in the $C_4$ to $C_7$ range seems to be pretty well established.

The complex formed from the adsorption of the isobutyl alcohol seems to behave differently from the iso-$C_4$ complex obtained by adding a carbon to the $C_3$ complex formed by the adsorption of isopropyl alcohol. The isobutyl alcohol complex yields a constant or nearly constant activity for the higher hydrocarbons, whereas in the isopropyl run the activity drops steadily from a value of 900 for the $C_4$ fraction to a value of 250 for the $C_{8.9}$ fraction.

***t*-Butyl Alcohol Run.**—In one run non-radioactive *t*-butyl alcohol was introduced into the inlet CO–$H_2$ gas stream at a concentration of 1.5%. The gaseous product was fractionated on a Podbielniak column and a small cut taken off bracketing the boiling point of neopentane. This cut was analyzed with a mass spectrograph; no neopentane (<0.1%) was found to be present. Apparently, the *t*-butyl alcohol will not build up into the hydrocarbon neopentane under Fischer–Tropsch synthesis conditions.

## Discussion

The question naturally arises as to whether one can conclude from the present results that primary alcohols are intermediates in the synthesis of higher hydrocarbons over iron catalysts. To arrive at an answer, let us first note the pattern of the build up of hydrocarbon on catalyst surfaces suggested by Weller and Friedel,[10] by Anderson, Friedel and Storch[11] and by Weitkamp, *et al.*[7b] They propose the following schematic representation of the way in which surface complexes build up on the catalyst surface



(1)

The dots indicate the points at which the next carbon group can attach itself. By assuming that the added carbon atoms go predominantly (90% of the time) onto the end carbons and only less frequently (10% of the time) onto the second carbon atom and by assuming that compounds containing quaternary carbon atoms are not formed, these various authors have been able to account for the branched chain–straight chain carbon distribution over the range of hydrocarbons extending from $C_4$ to about $C_{15}$.

It is at once evident that the experiments previously reported for ethyl alcohol fit into this pattern and suggest that the complex formed by adsorbing ethyl alcohol onto the surface is thereby an intermediate in the synthesis of higher hydrocarbons. This interpretation of the tracer experiments with ethyl alcohol is equivalent to considering an OH group as being attached to the $\alpha$-carbon in each of the above complexes and to postulating that successive carbons add 90% of the time to the $\alpha$-carbon and 10% of the time to the $\beta$-carbon atoms

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(8) The high radioactivity of the propane fraction fails to afford positive proof of the extensive adsorption of isopropyl alcohol because the propane formation might be caused by radioactive isopropyl alcohol molecules striking adsorbed hydrogen to form water and propane.

(9) P. H. Emmett and J. T. Kummer, *Proc. Third World Petroleum Congress*, Section IV, 15 (1951).

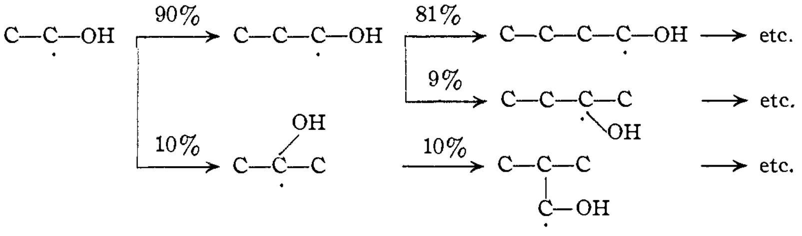
(10) S. Weller and R. A. Friedel, *J. Chem. Phys.*, **17**, 801 (1949).

(11) R. B. Anderson, R. A. Friedel and H. H. Storch, *ibid.*, **19**, 313 (1951).

when the OH groups of the complex are removed by hydrogenation. To conform to the experiments with radioactive ethyl alcohol the added carbon atoms could become chemisorbed to the metal surface as M=C=O and then join directly to the α- or β-carbon atom of the complex either before or after hydrogenation.

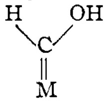
When one adds radioactive *n*-propanol in the synthesis one would expect on the above picture to obtain a $C_3$ complex leading to radioactive normal $C_4$ and iso-$C_4$ hydrocarbons in the 9:1 ratio in which they normally occur in syntheses. Actually, the *n*-propanol forms *n*-$C_4$ compounds almost exclusively. It follows, therefore, that *if* one assumes only one oxygen-containing $C_3$ complex in the actual synthesis, then the present experiments show that *n*-propanol will *not* form such a complex and hence is *not* an intermediate in the synthesis of higher hydrocarbons.

The facts suggest the following modification of the above reaction scheme



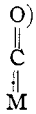
(2)

Here again a dot under the carbon labels the atom to which the next carbon atom will add. According to this scheme the complex formed by any primary alcohol may be considered to add an extra carbon from a



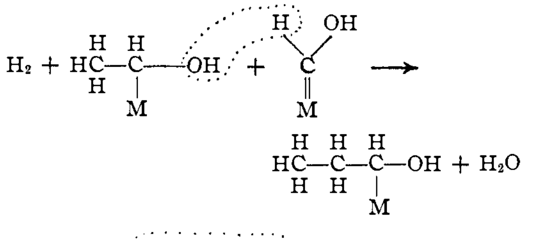
$$\mathrm{H(OH)C{=}M}$$

complex (rather than from

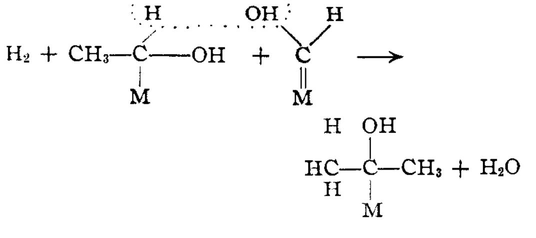


$$\mathrm{O{=}C{=}M}$$

) in one of two ways. This can be illustrated, for example, by the behavior of the adsorption complex of ethyl alcohol as



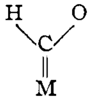
(3)



(4)

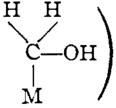
The complexes formed from the secondary alcohol have of course only one mode of attaching the next carbon atom as illustrated in the reaction scheme (2) above. One has only to assume that reaction (3) is nine times as likely as reaction (4) on the addition of each successive carbon atom to account for the observed hydrocarbon distribution actually observed in Fischer–Tropsch synthesis work. It is evident that this modified reaction scheme would lead one to expect that adsorbed *n*-propanol would form normal rather than iso-$C_4$ products and that isopropyl alcohol would, as observed, yield primarily iso-$C_4$ hydrocarbons. Accordingly, it is consistent with the results obtained in the present work. It is also in agreement with the observation of Weitkamp[12] to the effect that the propanol fraction from the products of synthesis over an iron catalyst was found to contain 10% isopropyl alcohol.[13] Unfortunately it does not account for the observation made in experiments with radioactive ethyl alcohol in which it was shown that about 10% of the carbon atoms added to the adsorbed $C_2$ alcoholic complex attached themselves to the β-carbon rather than to the α-carbon. If the reaction schemes proposed in equations 2, 3 and 4 in the present paper are correct, then an explanation will have to be found for the apparent attachment of about 10% of the added carbon atoms to the β-carbon rather than to the α-carbon. Possibly a small amount of structural isomerization of the $C_3$ hydrocarbon product might be taking place either during the synthesis run or during the pyrolytic analysis by which the position of the radioactive atoms was located in the $C_3$ hydrocarbon products.

Reaction schemes 2, 3 and 4 are substantially those postulated by Storch, Golumbic and Anderson.[14] Their proposed complex,



$$\mathrm{H(OH)C{=}M}$$

for adding carbon atoms has one other advantage worth mentioning. It differs from the complex



$$\left(\text{probably } \mathrm{H_2C(OH){-}M}\right)$$

which may be expected to form by the adsorption of methanol on the catalyst and which, as is evident from the smallness of the build up radioactivity per added carbon atom in the methanol run (Table II), seems relatively slow to build into the reaction chain to form higher hydrocarbons.

Finally, it is well to re-emphasize that the conclusions in the present paper are based on synthesis experiments with a 1:1 carbon-monoxide: hydrogen synthesis gas over singly promoted iron catalysts at one atmosphere pressure. It remains to be seen how the results with radioactive alcohols

[12] A. W. Weitkamp, paper delivered before the A.A.A.S. Gordon Conference, New London, N. H., June, 1949.

[13] It should be pointed out, however, that the ratio of the adsorbed primary to adsorbed secondary alcoholic complexes does not necessarily have to be the same as the ratio of the primary to secondary alcohols in the product. The agreement of the proposed ratio of primary to secondary alcoholic complexes on the catalyst surface with the ratio of primary propyl alcohol to secondary propyl alcohol in Weitkamp's experiments may be fortuitous.

[14] H. H. Storch, N. Golumbic and R. B. Anderson, "The Fischer-Tropsch and Related Syntheses," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 592.

as tracers would be influenced by changes in pressure, temperature, synthesis gas composition and catalyst composition.

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[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, HARVARD UNIVERSITY AND UNIVERSITY OF UTAH]

# The Inductive Effect and Chemical Reactivity. III. Effect of Charge Shifts on Energetics of Some Basic Reactions of Aliphatic Compounds[1]

BY RICHARD P. SMITH[2] AND HENRY EYRING

RECEIVED JANUARY 9, 1953

The effect of charge shifts due to induction on electronic energy in simple aliphatic molecules is discussed. It is shown that for a series of aliphatic hydrocarbons substituted by an electronegative substituent, R–X, the charge on X, as calculated by the inductive effect theory of Smith, Ree, Magee and Eyring,[3] is directly related to the stabilization energy of R–X, to the free radical resonance (stabilization) energy of the radical R·, and to the stabilization energy of the ion $R^+$, as well as to the stabilization energies of intermediate forms (as exist in activated complexes). This has considerable significance to relative organic equilibrium and rate constants, as is illustrated by several examples.

## Introduction

In the first paper of this series,[3] a semi-empirical theory was proposed for the inductive effect, and it was shown that magnitudes of small charge shifts due to induction may be estimated. The success of calculations of dipole moments of substituted methanes[3] and the correlation of activation energies with halogen charges for reactions of organic halides with sodium atoms[4] indicate that the theory is probably essentially correct, at least for the calculation of relative charge shifts in a series of similar molecules. The theory relates charge shifts to well-known bond polarizabilities, covalent bond radii and screening constants.

We now propose to discuss the effect of small charge shifts, due to the inductive effect, upon the energetics of a system. This will facilitate a discussion of the energetics of some chemical reactions of fundamental importance in terms of charge inductions which can be calculated by the method outlined in the first paper of this series. This paper is concluded with some specific examples illustrating the theory and clarifying the reasons for trends in some energies of dissociation and other processes.

## Theoretical Considerations

We have previously given a discussion of charge shifts in molecules in terms of the L.C.A.O. approximation to the M.O. method.[3] For a bond *a–b*, the expression for the net electronic charge on atom *a* was shown to be given approximately by

$$Q_a = \delta/\beta \qquad (1)$$

and is related to the electronegativity difference between *a* and *b* (see reference 3 for explanation of notation). Now in this same theory, neglecting the overlap integral, the energy of the bonding orbital is given by[5,6]

$$E = 1/2(\alpha_a + \alpha_b) - \sqrt{\delta^2 + \beta^2} \qquad (2)$$

so that a polar bond will be stabilized.

These results are well known, having been discussed a number of times in connection with the stabilization of *a–b* molecules over the average of *a–a* and *b–b* molecules,[7] *e.g.*, by Pearson.[6] The first term in (2), the average of the "coulombic integrals," $\alpha_i$, for the atoms, is taken to be the average of the bond energies of $a_2$ and $b_2$, and the remaining term, a function of the difference of the coulombic integrals, and always resulting in a lowering of the bond energy over this average, is assumed to account for the added stabilization due to the unsymmetrical character of the bond.

The situation discussed above for a chemical bond will be similar to the situation for a series of adjoining atoms. A hydrocarbon molecule, for example, may be represented as a series of connected orbitals of the type discussed above. The carbon–hydrogen bonds are well known to have little polarity. If, now, we replace one of the end hydrogens by a more electronegative element, such as chlorine, then, in accordance with the above discussion, charge will flow from the end carbon atom to the substituent. Now this removal of charge from the carbon atom will decrease the $\alpha$ integral for that atom, since the carbon nucleus will not be shielded so much; hence charge will, in turn, flow to this carbon atom from the atoms joined to the carbon, and so on.

In our theory of the inductive effect,[3] we merely developed a practical method for partially solving the above problem. Only the charge-distribution part of the problem was tackled. To calculate electron density changes, a rule given by Slater was used, that if the electronic charge on an atom is decreased a certain amount, the effective nuclear charge of that atom will be increased 0.35 of that amount (except for hydrogen, where 0.30 is used). The polarizability, a quantity which is known empirically for bonds, was introduced as a practical measure of the ease of transferring electronic charge from one atom to an adjacent one. As far as charge distributions are concerned, the inductive effect theory is a practical method for solving the charge distribution part of the quantum mechanical problem discussed above.

We now make some observations on the effect

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[1] Presented in part at the Conference on Reaction Mechanisms at Bryn Mawr College, Sept. 11, 1952.

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[3] R. P. Smith, T. Ree, J. L. Magee and H. Eyring, THIS JOURNAL, **73**, 2263 (1951).

[4] R. P. Smith and H. Eyring, *ibid.*, **74**, 229 (1952).

[5] R. S. Mulliken, *J. Chem. Phys.*, **3**, 573 (1935); *J. chim. phys.*, **46**, 497, 675 (1949).

[6] R. G. Pearson, *J. Chem. Phys.*, **17**, 969 (1949).

[7] L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1940.