TABLE I

| Compound | B. p. °C. | B. p. mm. | $n^{20}_D$ | | $d^{20}_4$ | | $MR_D$, obs. | $MR_D$, calcd. | Empirical formula | Analyses, % Calcd. C | Calcd. H | Found C | Found H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $BrCH_2CH(OC_4H_9)_2$ | 86.5 | 1 | 1.4477 | | 1.1511 | | 58.85 | 59.44 | $C_{10}H_{21}O_2Br$ | 47.43 | 8.36 | 47.42 | 8.53 |
| $Br_2CHCH(OC_4H_9)_2$ | 104 | 7 | 1.4750 | | 1.3937 | | 67.09 | 67.20 | $C_{10}H_{20}O_2Br_2$ | 36.16 | 6.07 | 36.44 | 6.20 |
| | | | | | | | | | | | | 36.56 | 6.57 |
| $BrCH{=}CHOC_2H_5$ | 41 | 14 | 1.4725 | | 1.4237 | | 29.73 | 29.61 | $C_4H_7OBr$ | 31.81 | 4.67 | 32.10 | 4.93 |
| $BrCH{=}CHOC_4H_9$ | 60 | 8 | 1.4660 | | 1.2744 | | 38.92 | 38.85 | $C_6H_{11}OBr$ | 40.23 | 6.19 | 40.34 | 6.34 |
| $HC{\equiv}COC_2H_5$ | 28 | 300 | 1.3812 | $1.3785^{25}$ | 0.7929 | $0.7874^{25}$ | 20.53 | 20.25 | $C_4H_6O$ | | | | |
| $HC{\equiv}COC_4H_9$ | 50.5 | 115 | 1.4053 | $1.4033^{25}$ | 0.8120 | $0.8078^{25}$ | 29.66 | 29.49 | $C_6H_{10}O$ | 73.41 | 10.27 | 73.19 | 10.28 |

with the boron trifluoride catalyst gave 0.33 g. of diethyl ether (40% yield) and 1.1 g. of the alcohol–ethyl acetate azeotrope, which corresponds to 0.75 g. of ethyl acetate (77% yield).

The table gives the physical constants and analyses of the new compounds prepared.

## Summary

Ethoxy- and butoxy-acetylene have been prepared from the corresponding bromoalkoxyethylenes. They are rather poisonous liquids which give unstable copper, silver and mercury derivatives. Their structures were proved by hydrogenation to the corresponding saturated ether and by hydrolysis to esters. They polymerize slowly at room temperature, but explode when heated in a sealed tube. Water adds more readily than to vinyl ethers, but less readily than to ketene acetal. Ethoxyacetylene may be refluxed with ethyl alcohol without reaction, but at 0° in the presence of a boron trifluoride–mercuric oxide catalyst and alcohol the products are diethyl ether and ethyl acetate. Ethyl orthoacetate gives the same products under like conditions.

LOS ANGELES, CALIFORNIA RECEIVED NOVEMBER 12, 1941

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, EMORY UNIVERSITY]

# A Kinetic Study of the Reactions of *n*-Butyl Bromide with the Sodium Salts of Phenol, Thiophenol and *n*-Butyl Mercaptan[1]

BY OSBORNE R. QUAYLE AND E. EARL ROYALS[2,3]

The reaction of sodium phenolate with *n*-butyl bromide in boiling alcohol requires from three to four hours for completion, while the corresponding reactions of sodium thiophenolate and sodium *n*-butyl mercaptide are essentially complete in a few seconds. There appears to be no previous quantitative work on these reactions, although similar reactions have been extensively studied. The reaction between methyl iodide and sodium ethylate was studied by Hecht, Conrad and Bruchner[4] who observed that the bimolecular rate constant is decreased by increasing initial concentrations of reactants. Segaller[5] made an extended study of the reactions of a series of normal and branched-chain alkyl iodides with sodium phenolate and observed the effects of temperature, concentration and solvent on the bimolecular rate constants. The rate constants were found to decrease with increasing initial concentrations of reactants, and no correlation was observed between reactivity and dielectric constant of the solvent. It was concluded that the reactions are "not ionic." The work of Hecht, Conrad and Bruchner and that of Segaller on the reaction of propyl iodide with sodium phenolate was repeated by Schroeder and Acree[6] as a test of their "dual hypothesis," according to which both ionic and molecular reactions proceed simultaneously and independently. The observed concentration effect was explained by this hypothesis. Lauer and Shingu[7] have recently studied the kinetics of the etherification reaction of allyl bromide with sodium phenolate with particular interest in concentration and solvent effects and conclude that the reaction is entirely ionic. Concentration effect is explained as due to a varying degree of solvation of the phenolate ion.

The object of this investigation was to deter-

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(1) The authors wish to express their gratitude to Dr. E. Emmet Reid, research consultant to the department, for suggesting the problem and for his continued interest and aid during its investigation.

(2) Abstracted from a thesis submitted by E. Earl Royals to the Graduate Faculty of Emory University in partial fulfillment of the requirements for the degree of Master of Science.

(3) Present address, University of Wisconsin, Madison, Wis.

(4) Hecht, Conrad and Bruchner, *Z. physik. Chem.*, **49**, 329 (1904).

(5) Segaller, *J. Chem. Soc.*, **103**, 1154 (1913); **103**, 1421 (1913); **105**, 106 (1914).

(6) Schroeder and Acree, *ibid.*, **105**, 2582 (1914), and previous papers.

(7) Lauer and Shingu, *Ber.*, **69**, 273 (1936).

mine the rate constants for each of the reactions under consideration under comparable conditions as a measure of the relative reactivities of the sulfur and oxygen compounds, to determine the effects of temperature, concentration, solvent and added salts on these rate constants and to use the data so obtained to postulate a mechanism for the reactions.

## Experimental

**Materials.**—Pract. *n*-butyl bromide was purified with concentrated sulfuric acid and was fractionated under reduced pressure; b. p. range 26.8–27.1° (42 mm.).

U. S. P. phenol was dissolved in dry ether and dried over anhydrous calcium chloride. The ether was evaporated and the phenol distilled at atmospheric pressure; b. p. range 179.0–179.5°.

Thiophenol and *n*-butyl mercaptan were purified by dissolving in sodium hydroxide solution, reprecipitating with hydrochloric acid and fractionating under reduced pressure; b. p. thiophenol 72.0° (27 mm.); b. p. range *n*-butyl mercaptan 55.0–56.0° (200 mm.).

Methyl and ethyl alcohols were dried by the method of Lund and Bjerrum.[8] Benzene was treated with concentrated sulfuric acid until no further coloration was produced, washed with water, dried over anhydrous calcium chloride and sodium and distilled through a short column at atmospheric pressure.

Lithium chloride was of reagent grade and was not further purified, but was dried in an oven at 100° for several days immediately before use.

**Procedure.**—Rate determinations were carried out in a thermostat maintained at 25.00, 35.00 and 42.40 ± 0.01°. Solutions of each reactant were made up to the desired molarity in volumetric flasks at the temperature of the thermostat. Ten-ml. portions of each reactant were pipetted into test-tubes, and the reactions allowed to run for measured time intervals, at the end of which they were stopped by pouring the contents of the tubes into an excess of standard hydrochloric acid. The tubes were closed with tight-fitting rubber stoppers. Extent of reaction was determined by back-titration with standard sodium hydroxide solution. Indicators used were methyl red–methylene blue for phenolate and *n*-butyl mercaptide titrations and brom phenol blue for sodium thiophenolate.

Volumetric solutions of sodium phenolate were prepared from stock solutions in absolute methyl and ethyl alcohols. Sodium thiophenolate and sodium *n*-butyl mercaptide solutions were prepared from weighed quantities of the mercaptans and stock solutions of sodium in absolute alcohol. *n*-Butyl bromide solutions were prepared from weighed quantities of the solute.

Initial concentrations were checked by titration of the volumetric solutions of sodium phenolate or mercaptide; one-half the molarity so obtained was taken as the initial concentration.

Precaution was taken to protect all solutions from moisture, and equipment used in rate determinations was dried in an oven at 180° for at least six hours immediately before use.

Where reactions were run in the presence of salts, the desired quantity of salt was added to the volumetric solution of sodium mercaptide. Reactions in mixtures of methyl alcohol and benzene were run by adding the desired volume of benzene to the volumetric solutions of reactants.

## Calculations

Rate constants were obtained graphically by plotting the function $x/a(a - x)$ against time, since initial concentrations of both reactants were the same in all reactions studied. Straight lines were obtained as shown by the data for a typical reaction in Table I.

TABLE I

REACTION OF PhSNa WITH *n*-BuBr AT 25.00°

| Time, min. | $a - x$ | $x/a(a - x)$ |
|---|---|---|
| 5 | 0.0741 | 3.624 |
| 5 | .0746 | 3.533 |
| 10 | .0575 | 7.520 |
| 10 | .0576 | 7.490 |
| 15 | .0475 | 11.18 |

$a$ = 0.1013 molar.

Energies of activation were obtained graphically by plotting log $k$ against the reciprocals of the absolute temperatures. Rate constants were reproducible to about 5%, and energies of activation may be considered as accurate to about ±1000 calories. Mole fractions of benzene were calculated on the assumption of no volume change on mixing.

## Results and Discussion

The rate constants obtained for the reactions of *n*-butyl bromide with the sodium salts of phenol, thiophenol and *n*-butyl mercaptan under various conditions of initial concentration, temperature and solvent and the energies of activation and the ratios of calculated to observed rate constants are

TABLE II

RATE CONSTANTS FOR REACTIONS OF SODIUM SALTS WITH *n*-BUTYL BROMIDE

| Reactant | Init. concn. | Solvent | Rate constant 25.0° | Rate constant 35.0° | Rate constant 42.4° | Energy of activation cal. | $\frac{k_{\text{calcd.}}}{k_{\text{obs.}}}$ |
|---|---|---|---|---|---|---|---|
| | | | $k \times 10^5$ | | | | |
| PhONa | 0.05 | $C_2H_5OH$ | 1.31 | 3.90 | 8.10 | 19,530 | 14.5 |
| PhONa | .10 | $C_2H_5OH$ | 0.992 | 3.18 | 8.07 | 21,990 | 17.2 |
| PhONa | .20 | $C_2H_5OH$ | .871 | 2.82 | 6.67 | 21,120 | 20.0 |
| PhONa | .10 | $CH_3OH$ | .401 | 1.32 | 3.48 | 22,940 | 1.4 |
| | | | $k \times 10^2$ | | | | |
| PhSNa | .05 | $C_2H_5OH$ | 1.28 | 3.42 | 6.57 | 17,400 | 66.7 |
| PhSNa | .10 | $C_2H_5OH$ | 1.25 | 3.12 | 5.54 | 15,720 | 76.9 |
| PhSNa | .20 | $C_2H_5OH$ | 1.24 | 2.84 | 4.75 | 14,060 | 83.3 |
| PhSNa | .10 | $CH_3OH$ | 0.450 | 1.10 | 2.25 | 17,840 | 4.8 |
| | | | $k \times 10^2$ | | | | |
| BuSNa | .05 | $C_2H_5OH$ | 2.00 | 5.10 | 8.94 | 16,800 | 8.7 |
| BuSNa | .10 | $C_2H_5OH$ | 1.81 | 4.84 | 8.84 | 17,540 | 9.1 |
| BuSNa | .20 | $C_2H_5OH$ | 1.83 | 4.50 | 7.58 | 15,900 | 9.7 |
| BuSNa | .10 | $CH_3OH$ | 0.443 | 1.11 | 2.00 | 17,140 | 20.4 |

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[8] Lund and Bjerrum, *Ber.*, **64**, 210 (1931).

given in Table II. Calculated values were obtained from the expression $k = 2.8 \times 10^{11} se^{-E/RT}$ by substitution of average experimental values of $E$. The value $2.8 \times 10^{11}$ is an average value of theoretical collision frequencies for a number of solution reactions.(9)

**Comparison of Sulfur–Oxygen Reactivity.**—The order of reactivity of the three sodium, salts with *n*-butyl bromide is butyl mercaptan, sodium thiophenylate, sodium phenolate. The difference in reactivity of the two sulfur compounds is small; rate constants in methyl alcohol solution are the same within experimental error, while those in ethyl alcohol solution differ by a factor of about 1.5. No significant difference in activation energies is apparent. Assuming constancy of $s$, a factor of 1.5 in the rate expression $k = se^{-E/RT}$ corresponds to a change in $E$ of roughly 300 calories. Such a difference is well within the experimental error of the present research.

The rate constants characteristic of sodium phenolate and sodium thiophenolate differ tremendously. The sulfur compound is approximately 1000 times as reactive toward *n*-butyl bromide as is the analogous oxygen compound. In both methyl and ethyl alcohol solutions, the difference in activation energies is about 5000 calories.

The agreement between calculated and observed rate constants is within the normal range to be expected considering the approximate nature of the calculations. This indicated that despite the great difference in reactivity between analogous oxygen and sulfur compounds, the same mechanism obtains in both cases.

**The Effect of Initial Concentration.**—In general, there is about a 15 to 20% decrease in rate constant as the initial concentration is increased from 0.05 to 0.20 molar. A concentration effect of this nature is customarily taken as evidence that the reaction under consideration is ionic in nature and that the rate constant is dependent upon the degree of ionization. The "dual hypothesis" of Schroeder and Acree[6] has offered the most suitable and generally accepted(10) mechanism of etherification reactions yet proposed. Legitimate objections to this hypothesis, however, have been raised[7] on the basis that sodium salts of phenols are strong electrolytes in alcoholic solution and that, consequently, the degree of ionization as given by the ratio $\Lambda/\Lambda_0$ has no theoretical significance. Recent work(11) on the conductivity behavior of non-aqueous solutions indicates that strong electrolytes in alcoholic solution are best considered as completely ionized. Deviations from the behavior expected of completely dissociated salts are to be explained on the basis of interionic attractions.

It will be observed that in the reactions considered in this research the ionic strength of the system remains constant provided there is no precipitation of sodium bromide

$$PhO^- + Na^+ + BuBr = PhOBu + Na^+ + Br^-$$

The ionic strength is at all times numerically equal to the initial concentration of sodium phenolate or mercaptide.

**The Effect of Neutral Salts.**—The effect of added salts on the reaction of sodium *n*-butyl mercaptide with *n*-butyl bromide in 0.05 molar initial concentration in ethyl alcohol solution at 35.0° is shown in Table III. It will be observed that the neutral salt effect is of the same sign as the initial concentration effect and is comparable in magnitude.

TABLE III

SALT EFFECT ON THE REACTION OF *n*-BuSNa WITH *n*-BuBr IN ETHYL ALCOHOL AT 35.0°

| Concentration of LiCl, moles/liter | $k \times 10^2$ | Concentration of PhONa, moles/liter | $k \times 10^2$ |
|---|---|---|---|
| 0.0000 | 5.10 | 0.0000 | 5.10 |
| .0197 | 4.87 | .0168 | 5.25 |
| .0333 | 4.78 | .0336 | 4.79 |
| .0456 | 4.48 | .0587 | 5.07 |
| .0680 | 4.35 | .0839 | 4.98 |

**The Solvent Effect.**—All reactions studied are faster in ethyl alcohol than in methyl. The rate constant for the reaction of sodium *n*-butyl mercaptide with *n*-butyl bromide in 0.10 molar benzene solution at 35.0° was determined by extrapolation of the data obtained in methyl alcohol–benzene mixtures. The results are plotted in Fig. 1. In Table IV the data on this particular reaction in three solvents are summarized. The

TABLE IV

THE REACTION OF *n*-BuSNa WITH *n*-BuBr AT 35.0°

| Solvent | Dielectric constant | $k \times 10^2$ | Relative $k$ | Energy of activation |
|---|---|---|---|---|
| $C_6H_6$ | 2 | 0.12 | 1.00 | .... |
| $CH_3OH$ | 32 | 1.11 | 9.25 | 17,140 |
| $C_2H_5OH$ | 26 | 4.84 | 40.33 | 16,750 |

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(9) Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford Univ. Press, Oxford, 1933, p. 78.

(10) Moelwyn-Hughes, *ibid.*, p. 104.

(11) Kraus, *J. Chem. Ed.*, **12**, 567 (1935); Davidson, *ibid.*, **14**, 218 (1937).

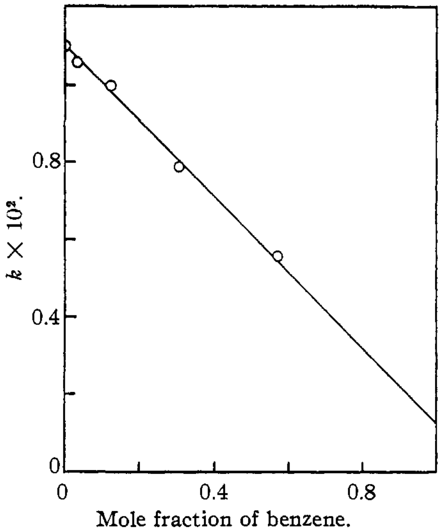

Fig. 1.—Rate of reaction of sodium *n*-butyl mercaptide with *n*-butyl bromide in benzene–methyl alcohol mixtures at 35.0°.

rate constants with the two alcohols as solvents show increasing value with decreasing dielectric constant in accord with the predictions of Eyring.[12] This behavior, however, does not extend to benzene as solvent.

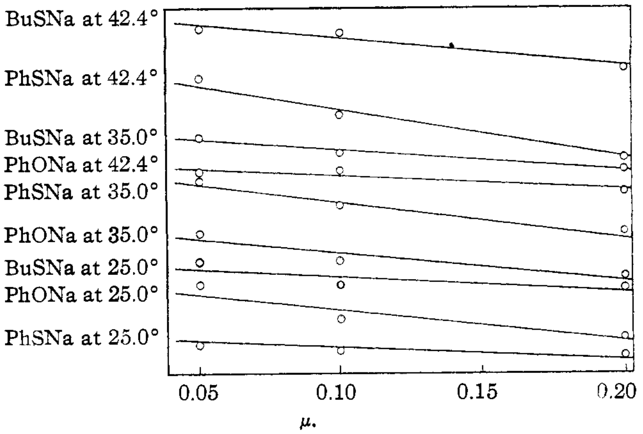

Fig. 2.—Variation of rate constants with ionic strength. Ordinates have been shifted to conserve space and avoid confusion of points.

**General Discussion.**—The similarity between observed concentration and salt effects indicates that total electrolyte concentration, or ionic strength, determines the rate constant for a given etherification reaction in solvents of high dielectric constant, such as methyl and ethyl alcohols. In such solvents the reactions are best considered as occurring between the phenolate or mercaptide ion and the alkyl halide molecule. The process may be pictured

$$RO^- + C—X \rightleftharpoons RO^-—^+C^+—X^- \longrightarrow RO—C + X^-$$

The reaction is facilitated by an electron drift toward the carbon atom from the RO group. On this basis, the substitution of sulfur for oxygen should result in greatly enhanced reactivity, since sulfur is electropositive relative to oxygen. The relative reactivities of the *n*-butyl mercaptide and thiophenolate ions are explained on the same basis, since the phenyl group is electronegative relative to an alkyl group. The electron drift effect induced by the *R* group is of relatively small magnitude as compared to the effect of the relative electronegativity of the bound ion.

It has been demonstrated[12] that in reactions of this type linearity should be observed between log *k* and the ionic strength. The data obtained in this research with ethyl alcohol as solvent have been plotted in this manner in Fig. 2. The ionic strength used here is numerically equal to the initial concentrations of reactants in each case. The comparison between concentration and salt effects for the reaction of sodium *n*-butyl mercaptide with *n*-butyl bromide is shown graphically in Fig. 3. The ionic strength employed in plotting the salt effect is the sum of the molar concentrations of sodium *n*-butyl mercaptide and added salt. It is apparent from Fig. 3 that the effect of lithium chloride becomes considerably more pronounced than the concentration effect at high ionic strengths. It must be remembered that with the concentrations of lithium chloride employed, the solutions were very near to saturation with respect to sodium chloride

$$\text{LiCl} + \text{BuSNa} = \text{BuSLi} + \text{NaCl}$$

The effect of sodium phenolate, as might be expected from its greater solubility in alcohol than

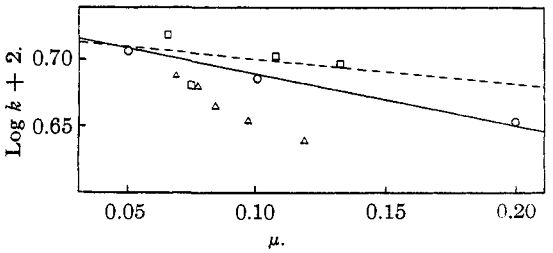

Fig. 3.—Effects of neutral salts and initial concentration on the reaction of sodium *n*-butyl mercaptide with *n*-butyl bromide in 0.05 molar initial concentration in ethyl alcohol at 35.0°: ○, concentration effect; △, effect of LiCl; □, effect of PhONa; ——, concentration effect; ----, effect of PhONa.

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[12] Laidler and Eyring, *Ann. N. Y. Acad. Sc.*, XXXIX, Art. 5, pp. 303–335.

either lithium or sodium chloride, more nearly coincides with the effect of initial concentration.

According to the predictions of Eyring,[12] provided the ionic mechanism persists, the reaction of sodium *n*-butyl mercaptide with *n*-butyl bromide should proceed more rapidly in alcohol–benzene mixtures than in pure alcohol. It is evident from Fig. 1 that in methyl alcohol–benzene mixtures the rate constant decreases with increasing mole fraction benzene, but does not appear to approach zero in pure benzene. This indicates that an ion-pair reaction comes into play in alcohol–benzene mixtures in addition to the ionic reaction. The ion-pair reaction requires a much higher activation energy than the ionic reaction, since there is involved a separation of the ion-pair against a strong electrostatic attraction.

It appears, then, that the etherification reactions studied here are capable of proceeding by two distinct mechanisms depending on the nature of the solvent. In solvents of high dielectric constant the reactions are ionic, in solvents of very low dielectric constant an ion-pair mechanism predominates, while in solvents of moderate dielectric constant both mechanisms are involved, and the measured rate constant depends on the fraction of total reaction occurring by each mechanism.

## Summary

1. The rates of reaction of *n*-butyl bromide with the sodium salts of phenol, thiophenol and *n*-butyl mercaptan have been determined under comparable conditions, and activation energies have been determined with both methyl and ethyl alcohols as solvents.

2. The order of reactivity with *n*-butyl bromide was found to be BuSNa > PhSNa > PhONa.

3. Rate constants were found to decrease with increasing initial concentration of reactants.

4. Neutral salts were found to exert an effect similar in sign and magnitude to the initial concentration effect.

5. The order of reactivity of sodium *n*-butyl mercaptide with *n*-butyl bromide in different solvents, other factors being comparable, was found to be $C_2H_5OH > CH_3OH > C_6H_6$.

6. A mechanism for the reactions is postulated and discussed in the light of the experimental data and certain theoretical considerations.

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[CONTRIBUTION FROM THE CENTRAL EXPERIMENT STATION, BUREAU OF MINES, U. S. DEPARTMENT OF THE INTERIOR]

# Kinetics of Hydrogen Consumption, Oxygen Elimination and Liquefaction in Coal Hydrogenation. Nature of the Catalytic Reactions[1]

BY H. H. STORCH, C. O. HAWK, AND W. E. O'NEILL

In previous papers of this series[2,3,4] on coal hydrogenation in the presence of a stannous sulfide catalyst, the rates of change of readily measurable quantities (namely: hydrogen absorbed, oxygen removal as water and carbon oxides, and solubility in benzene) were determined. The temperature coefficient of the rate of hydrogen absorption was relatively low, and the rate appeared to be independent of those of oxygen elimination and liquefaction. It was assumed, therefore, that the slow step in the hydrogen consumption was the diffusion of hydrogen through a liquid film on the catalyst surface. As will be shown below, additional data and a more careful analysis show that the nature of the rate-determining step varies with the temperature.

From the earlier work[2] on the rates of oxygen removal and of liquefaction at various temperatures in the presence of a stannous sulfide catalyst, four stages in the coal-hydrogenation process could be discerned, namely:

(a) Solution or extraction of the coal. This is practically the only process occurring at a moderate, measurable rate below 370°. Its temperature coefficient is about 1.2/15°, and the slow step is probably a depolymerization of the coal by solvation.

(b) A primary decomposition of the coal at temperatures above 370° involving the rapid elimination of about 60% of the oxygen of the

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[1] Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

[2] H. H. Storch, C. H. Fisher, A. Eisner and L. Clarke, *Ind. Eng. Chem.*, **32**, 346–53 (1940).

[3] C. H. Fisher, G. C. Sprunk, A. Eisner, L. Clarke, M. L. Fein and H. H. Storch, *Fuel*, **19**, 13–16, 51–55, 67–69 (1940).

[4] C. H. Fisher, A. Eisner, L. Clarke, M. L. Fein and H. H. Storch, *ibid.*, **20**, 5–13 (1941).