amine (9.5 g., 0.038 mole) was added gradually to 30 ml. of purified thionyl chloride. After the initial vigorous reaction had subsided the mixture was refluxed for one hour, and the excess thionyl chloride removed under reduced pressure. The residue was recrystallized from absolute ethanol. The data on this compound and the other members of the series are summarized in Table II.

Summary

1. Several heterocyclic analogs of dibenzylaminoethyl chloride have been prepared for testing as sympatholytic agents.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

A Study of Some Condensations of *o*-Methylolphenol

BY MURRAY M. SPRUNG AND MATTHEW T. GLADSTONE

The processes which occur during the formation of phenolaldehyde resins have been well systematized in recent years.[1] It is now generally agreed that three basic types of reactions occur: (1) Addition of aldehyde (formaldehyde) ortho or para to a phenolic hydroxyl group gives, as the simplest recognizable product, a methylol phenol.[2] (2) Condensation with a second molecule now gives a dinuclear reaction product. Repetition of these addition and condensation steps then yields polynuclear reaction products of varying structures, chain lengths and degrees of branching, depending upon the structures of the reactants and the conditions imposed upon them. (3) More complex condensations and rearrangements of these intermediates finally are involved, leading, usually at higher temperatures, to complex, highly condensed structures.

Despite the wealth of chemical evidence adduced in support of the above generalizations, relatively little use has been made of kinetics in the study of phenol-aldehyde resinification. Such attempts have indeed been discouraged by the heterogeneous nature of the phenomena involved and by the lack of simple or distinctive analytical tools. Previous efforts have in general concerned themselves with the so-called primary (addition) reactions alone; or have involved measurements of the rates of many consecutive or integrated processes involved in resinification or in resinification and "curing" combined.[3]

Several years ago, there was reported[4] the reaction between various phenols and paraformaldehyde in virtual absence of water or other solvent and with triethanolamine as catalyst. The disappearance of formaldehyde under these conditions (the addition step, 1) apparently followed a first order rate law. Preliminary attempts to estimate the rates of the condensation reactions (step 2) were also described. It was observed that the condensation reactions are relatively slow compared to formaldehyde addition, and that phenols which readily form methylol derivatives also undergo subsequent condensations with relative ease.

Nordlander's extensive studies[3g] of the ammonia catalyzed reaction between phenol and formaldehyde indicated first order kinetics over a wide range of concentrations of reactants and catalysts. In contrast, most other aqueous alkaline catalyzed reactions show second order kinetics.[5] von Euler and Kispeczy[6] studied 2,4- and 2,6-dimethyl phenol in each of which only one position is available for reaction. With formaldehyde, in aqueous ethanol with hydrochloric acid as catalyst, second order kinetics were observed. A specific rate constant some 75% greater was observed for phenol under similar conditions.

Recently Jones[7] reported on the initial phases of the phenol–formaldehyde reaction. Under acidic conditions, second order rates were observed between 80 and 100°, but a reversion to first order at low temperatures (30°) was noted. In presence of alkali (NaOH) the reactions were first order during the first 45% at 40°. (This interpretation, however, has been criticized by Goldblum.)[8]

In the present work the starting material is *o*-methylol phenol (saligenin) a crystalline substance which can easily be obtained pure by a method independent of aldehyde addition. This effectively eliminates step (1) in the generalized reaction scheme. Its reactions with itself, with phenol and with resorcinol have been studied under a variety of conditions.

Materials.—Saligenin was obtained from Hynson, Westcott and Dunning, Inc., as a colorless, crystalline solid (produced by catalytic reduc-

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(1) (a) Zinke and co-workers, *Ber.*, **77B**, 264 (1944), and previous articles; (b) H. v. Euler and co-workers, *Arkiv. Kemi Mineral. Geol.*, **15A**, No. 11 (1942), and previous articles; (c) K. Hultzsch and co-workers, *Ber.*, **75B**, 363 (1942), and previous articles; (d) T. S. Carswell, "Phenoplasts," pages 12–29. Dr. Carswell has presented an admirable summary of much of the above and pertinent related material.

(2) Hemi-acetals (hemi-formals) may apear as precursors, but no unequivocal demonstration of their presence or of the role they play has yet been given.

(3) (a) Novak and Cech, *Ind. Eng. Chem.*, **20**, 796 (1928); (b) Megson, *J. Soc. Chem. Ind.*, **57**, 189 (1938); **58**, 131 (1939); (c) Holmes and Megson, *ibid.*, **52**, 415T (1933); (d) Granger, *Ind. Eng., Chem.*, **29**, 1305 (1937); (e) Tsuruta, *J. Soc. Chem. Ind. Japan*, **40**, 125B (1937); (f) Dubrisay, *Ind. Plastiques*, **1**, 132 (1945); (g) Nordlander, *Oil, Paint, Drug Rept.*, **130**, *3*, 27 (1936).

(4) M. M. Sprung, THIS JOURNAL, **63**, 334 (1941).

(5) K. B. Goldblum, private communication.

(6) von Euler and Kispeczy, *Z. physik. Chem.*, **A189**, 109 (1941).

(7) T. T. Jones, *J. Soc. Chem. Ind.*, **65**, 264 (1946).

(8) K. B. Goldblum, *J. Soc. Chem. Ind.*, in press.

tion of salicylaldehyde). It was crystallized from ethylene dichloride until a constant melting point of 83.5–84.0° was attained. U.S.P. phenol was redistilled and a middle cut taken, m. p. 41.5–42.0°. Merck reagent grade resorcinol was used directly when it showed the proper bromine equivalent; otherwise it was crystallized from water until analytically pure.

The triethanolamine was Merck purified grade. The tetraethylammonium hydroxide was a 40% aqueous solution obtained from E. I. du Pont de Nemours and Company. No purification of this solution was attempted; its strength was checked titrimetrically. The sodium hydroxide was Eimer and Amend reagent grade. All analytical reagents were prepared from reagent grade chemicals and standardized by common analytical procedures.

Analytical Method.—After consideration of several alternate procedures, bromination, despite its known limitations, was adopted as the most practical of available analytical tools. The method used is essentially that described in an earlier paper.[9] However, the standard conditions of the earlier work (which lead to constant fractional over-bromination of ortho and para alkyl substituted phenols) were modified so as to achieve virtually quantitative bromination at unsubstituted ortho and para positions and, concomitantly, quantitative elimination of ortho and para methylol groups.[10]

Optimum conditions are specified as follows: Between 0.32–0.35 g. of the mixture of phenols is dissolved, using 10–15 ml. of 1 *N* aqueous sodium hydroxide, and the solution is diluted to 250 ml. in a volumetric flask. A 25-ml. aliquot is transferred to a 250-ml. ground-glass stoppered iodination flask. To this is added 25 ml. of 0.1 *N* potassium bromate–potassium bromide solution and the walls are washed down with 50 ml. of water. Then 2.5–3.0 ml. of concentrated hydrochloric acid is added (in such a manner as to prevent bromine from escaping) and the mixture is allowed to stand ten minutes with occasional shaking. Ten ml. of 10% potassium iodide is then carefully added and the mixture allowed to stand ten minutes longer, with occasional shaking. The liberated iodine is titrated with 0.1 *N* sodium thiosulfate, using starch indicator.

The weight of sample must be within the limits given to achieve quantitative bromination and replacement of methylol groups, yet avoid over-bromination when reactive methylene groups are present. Under the conditions outlined no significant over-bromination was observed up to at least 80% conclusion of the reactions whose progress was being followed.

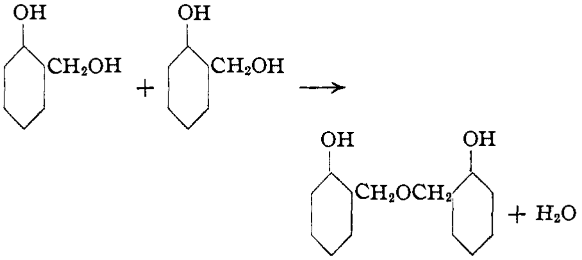
The analytical method requires that relatively small differences in substitution capacity (bromination) be measured. This difficulty is aggravated by the slow rate at which the resin forming reactions involved proceed in dilute solution. Therefore it has been necessary, as in previous work in this field, to work with highly concentrated solutions, or in absence of diluents. The results so obtained naturally do not conform strictly to classical kinetic concepts. Further, because of the viscous nature of the solutions or melts, weight samples have been taken, as in the previous work.[4] Concentrations are therefore expressed in moles per 1000 g. rather than in moles per liter. (Density changes during the course of the reaction are, however, actually not important.)

The analytical results are calculated using the formula $r = 0.005\ NVM/W$ where N, V, and W are the normality of the thiosulfate, the net volume of thiosulfate in milliliters, and the weight of the sample in grams; and M is the molecular weight of the monomeric phenol or the average molecular weight of mixed phenolic reactants.

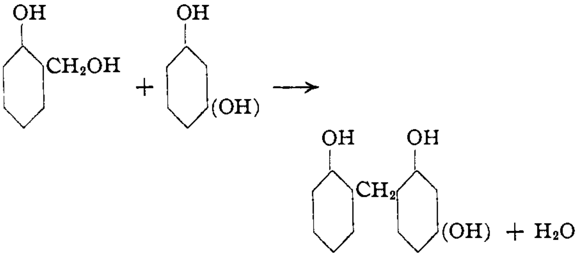
Determination of Reaction Order.—The order of the reaction with respect to the methylol phenol (saligenin) was obtained in the usual manner by plotting − log (saligenin) *vs.* time for first order and 1/(saligenin) *vs.* time for second order.

The concentration of saligenin in the uncatalyzed reactions is calculated by assuming these equations to be valid

I Self-condensation of saligenin



II Condensation of saligenin with resorcinol or phenol



If "*x*" is the concentration of product formed, "2*x*" is the concentration of mononuclear phenolic rings in the product, and "*a*" the initial concentration of saligenin, then, since it is postulated that no over-bromination occurs and that methylol groups are completely replaced by bromine, "*r*" (the number of reactive positions per mono-

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[9] Sprung, *Ind. Eng. Chem., Anal. Ed.*, **13**, 35 (1941).

[10] (a) Francis, THIS JOURNAL, **48**, 1631 (1926); (b) v. Euler and Kispeczy, ref. 6; (c) Ruderman, *Ind. Eng. Chem., Anal. Ed.*, **18**, 753 (1946); (d) Sprung, ref. 9.

TABLE I

EXPERIMENTAL RESULTS

Reactants	Run no.	Temp., °C.	Catalyst	Product	Order	Rate constant, *k*
Saligenin	60, 65	98.5	None	"Salireton"[f]	2nd	7.2×10^{-4} kg./mole/min.
Saligenin	11	109	None	"Salireton"[f]	2nd	1.53×10^{-3} kg./mole/min.
Saligenin	22	119	None	"Salireton"[f]	2nd	2.64×10^{-3} kg./mole/min.
Saligenin	12	130.5	None	"Salireton"[f]	2nd	5.96×10^{-3} kg./mole/min.
Saligenin	78, 24	98.5	T. E. A.[a,d]	Resin	1st	2.8×10^{-3}/min.
Saligenin	58	98.5	T. E. A.[b]	Resin	1st	2.25×10^{-3}/min.
Saligenin	59	98.5	T. E. A.[c]	Resin	1st	2.25×10^{-3}/min.
Saligenin	85	110.5	T. E. A.[a]	Resin	1st	6.1×10^{-3}/min.
Saligenin	82	118	T. E. A.[a]	Resin	1st	1.07×10^{-2}/min.
Saligenin	14	130.5	T. E. A.[a]	Resin	1st	1.66×10^{-2}/min.
Saligenin	66	98.5	NaOH[a]	Resin	1st	2.6×10^{-3}/min.
Saligenin	67	98.5	Q. B.[a,e]	Resin	1st	2.6×10^{-3}/min.
Saligenin:pinacol (1:2)	5	98.5	None	"Salireton"	2nd	2.35×10^{-4} kg./mole/min.
Saligenin:pinacol (1:1)	48	98.5	T. E. A.[c]	Resin	1st	5.75×10^{-4}/min.
Saligenin:pinacol (1:2)	49	98.5	T. E. A.[a]	Resin	1st	3.8×10^{-4}/min.
Saligenin:pinacol (1:3)	50	98.5	T. E. A.[a]	Resin	1st	2.7×10^{-4}/min.
Saligenin:phenol (1:1)	61, 70	98.5	None	Dihydroxydiphenylmethane	2nd	4.1×10^{-4} kg./mole/min.
Saligenin:phenol (1:1)	45, 15	98.5	T. E. A.[c]	Dihydroxydiphenylmethane	2nd	5.13×10^{-4} kg./mole/min.
Saligenin:phenol (1:1)	81	110.5	T. E. A.[a]	Dihydroxydiphenylmethane	2nd	1.51×10^{-3} kg./mole/min
Saligenin:phenol (1:1)	84	118	T. E. A.[c]	Dihydroxydiphenylmethane	2nd	2.35×10^{-3} kg./mole/min.
Saligenin:phenol (1:2)	46, 20	98.5	T. E. A.[a]	Dihydroxydiphenylmethane	2nd	4.51×10^{-4} kg./mole/min.
Saligenin:resorcinol (1:1)	10	98.5	None	Trihydroxydiphenylmethane	2nd	3.28×10^{-3} kg./mole/min.
Saligenin:resorcinol: Pinacol (1:1:2)	17	98.5	None	Trihydroxydiphenylmethane	2nd	1.06×10^{-3} kg./mole/min.
Saligenin:resorcinol: Pinacol (1:2:2)	19, 25	98.5	None	Trihydroxydiphenylmethane	2nd	1.91×10^{-3} kg./mole/min.
Saligenin:resorcinol: Pinacol (2:1:2)	21	98.5	None	Trihydroxydiphenylmethane	2nd	2.18×10^{-3} kg./mole/min.
Saligenin:resorcinol: Pinacol (1:1:2)	18	98.5	T. E. A.[c]	Trihydroxydiphenylmethane	2nd	1.18×10^{-3} kg./mole/min.
Saligenin alone for 300	16	98.5	None	"Salireton"	2nd	5.85×10^{-4} kg./mole/min.
minutes then T. E. A. added		98.5	T. E. A.[a]	Resin	1st	3.8×10^{-4}/min.

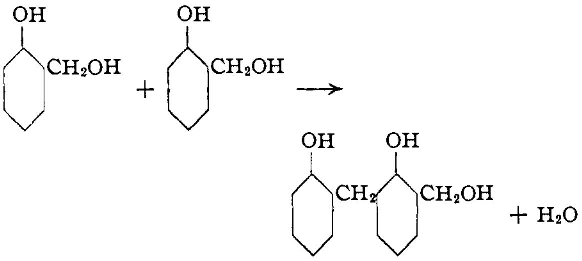
[a] 0.174 mole/1000 g. [b] 0.348 mole/1000 g. [c] 0.696 mole/1000 g. [d] T. E. A. is triethanolamine. [e] Q. B. is tetraethylammonium hydroxide. [f] Salireton is 2,2'-dihydroxydibenzyl ether.

nuclear phenolic ring) will be found as follows

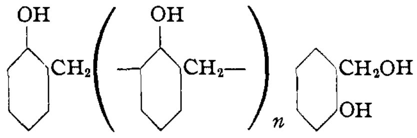
$$r = \frac{3(a-x) + 3(a-x) + 4x}{2a - 2x + 2x} = \frac{3a - x}{a}$$

from which $x = a(3 - r)$ and $a - x = a(r - 2)$. Because of the nature of the bromination reaction this expression is valid both for self-condensation of saligenin and for its reaction with either phenol or resorcinol.

III. For the catalyzed self-condensation of saligenin the following equation is initially assumed to be applicable



i. e., it is assumed that a methyloldihydroxydiphenylmethane is the first product of the reaction. Actually, in time, this reaction goes much further (in the direction of polymer formation). Near completion the product is a polymer, the structure of which may be represented, typically, as



The value of "r" approaches unity in the limiting case. However, as an approximate solution for this problem, it is assumed that for values of "r" appreciably greater than 2, there are negligible amounts of species of higher molecular weight than the dimer present. Since the dimer has four positions reactive toward bromine, the calculation given above may similarly be applied to the early phase of the catalyzed reaction.

Experimental Results and Discussion

A summary of experimental results is contained in Table I. Included are data concerning the condensation of saligenin with itself, with phenol and with resorcinol at temperatures between 98.5 and 130.5°, both in presence and absence of catalysts. In most cases the system studied contained no solvent, but in a number of runs pinacol was used as a diluent.[11]

The rate constants in Table I have been calculated from the observed slopes of the rate curves in Figs. 1, 3, 6, 8, 9 and 10. In those cases where a plot of t *vs.* $1/(r - 2)$ is shown, it was, of course, necessary to divide by "a" (the

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[11] Pinacol almost uniquely fits the requirements for a diluent for this system: it is a highly polar solvent which is unreactive toward the major components involved and toward the reagents used in the analytical procedure.

initial concentration of reactants in moles per 1000 g.) to obtain the correct values for "*k*."

Uncatalyzed Self-Condensation of Saligenin.—The calculated data for this series of runs are shown in Figs. 1 and 2. In absence of solvent, the reaction is of apparent second order, with an activation energy of about 20,000 cal./mole. One run, in the presence of two moles of pinacol per mole of saligenin, also showed second order kinetics. The reaction product was isolated after the conclusion of a number of runs, and demonstrated to be the simple ether, (2,2'-dihydroxydibenzyl ether ("salireton"). A sample was crystallized two times from hexane–benzene; m. p. 119–20°; m. p. of dibenzoate (from benzoic anhydride in pyridine), 114–115°; Ziegler and Lercher[12] reported 115°.

Anal. Calcd. for $C_{14}H_{14}O_3$ (2,2'-dihydroxydibenzyl ether): C, 73.0; H, 6.13. Found: C, 73.3; H, 6.45.

This ether has previously been shown by Ziegler and Lercher[12] to be the chief product obtained on heating saligenin at temperatures in the neighborhood of 140–200°. However, maximum yields of around 16% were thus obtained, whereas in one run continued under the present conditions for a longer period than normal, well over 80% of the theoretical yield of the ether was obtained. Thus, it is reasonably certain that the reaction is fairly free from complications under these conditions.

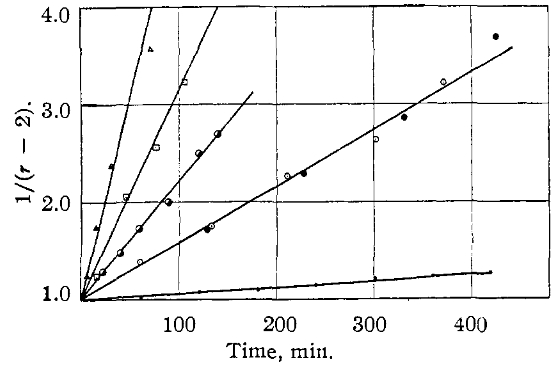

Fig. 1.—Self-condensation of saligenin in the absence of catalyst: ●, run 60, 99°; ⊙, run 65, 99°; ◑, run 11, 109°; ⊡, run 22, 119°; ◬, run 12, 130.5°; •, run 5, 1 saligenin:2 pinacol at 99°.

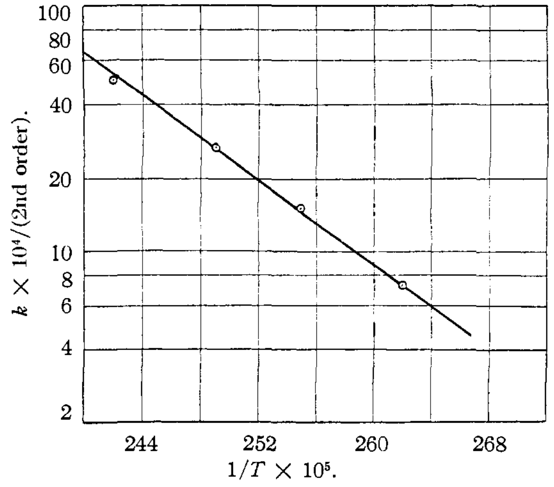

Fig. 2.—Self-condensation of saligenin in the absence of catalyst: variation of specific rate constant with the reciprocal of the absolute temperature.

Catalyzed Self-Condensation of Saligenin.—In the presence of catalytic amounts of triethanolamine, the reaction of saligenin with itself obeys first order rather than second order kinetics. The reaction product is no longer 2,2'-dihydroxydibenzyl ether, but is a sirupy liquid in the early stages of the reaction, which changes gradually to a resinous solid. Pure components

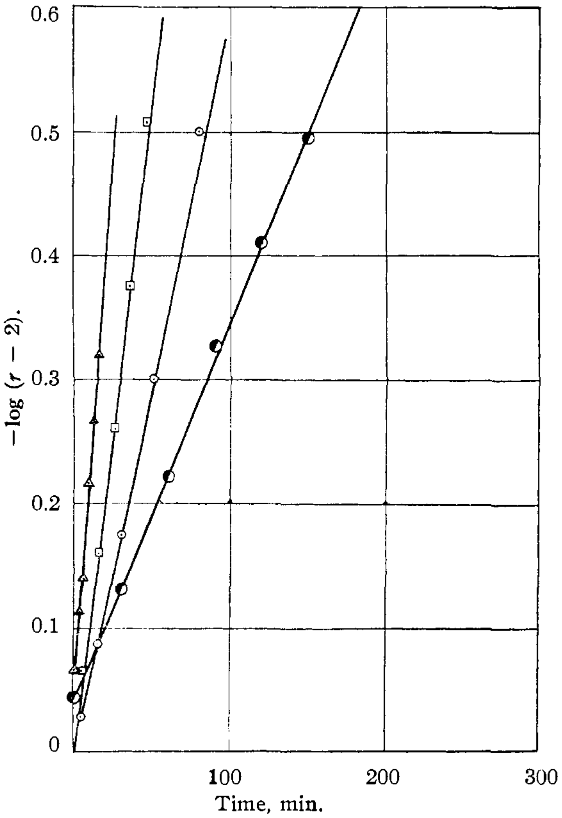

Fig. 3.—Self-condensation of saligenin in the presence of triethanolamine: ◐, run 24, 99°; O, run 85, 110.5°; ⊡, run 82, 118°; △, run 14, 130.5°.

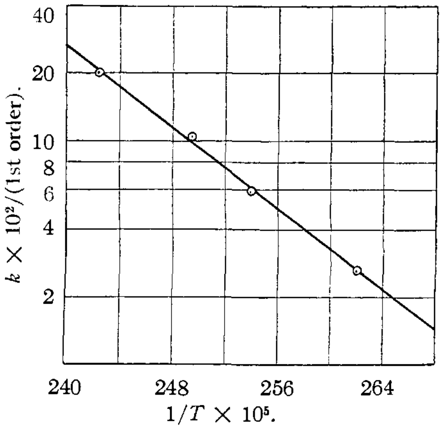

Fig. 4.—Self-condensation of saligenin in the presence of triethanolamine: variation of specific rate constant with the reciprocal of the temperature.

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(12) Ziegler and Lercher, *Ber.*, **74B**, 841 (1941).

have not been isolated. Data obtained between 99 and 130.5° (shown in Figs. 3 and 4) have been calculated on the assumption, stated previously, that only the first stage in a supposedly stepwise reaction need be considered. An activation energy of about 18,500 cal./mole is calculated from these data. No discernible change in order occurs on adding, one, two, or three moles of pinacol per mole of saligenin (Table I, runs 48, 49 and 50). However, a definite medium effect is encountered, since the specific rate constant, which decreases in proportion to the amount of solvent used, cannot be extrapolated to zero solvent concentration.

The data from several runs carried out in the presence of different bases or differing concentrations of base are combined in Fig. 5. Although the points scatter considerably, they all fall on a single straight line, within the maximum limits of error of the experimental technique (0.03 bromine equivalent). This plot thus brings into focus the interesting result that the rate of alkaline saligenin condensation is essentially independent of the strength of the base used and also, within limits, of the concentration of base. Similar observations have been noted previously; for example, by Granger,[13] but this is the first time to our knowledge that the effect has been demonstrated quantitatively. It is true, of course, that at some low alkali concentration the reaction should be of mixed order and the product should be a mixture of the ether and resin. The conditions under which this occurs have not as yet been established.

An implication of much of the earlier work in this field is that dibenzyl ethers are intermediates in the transition of methylol phenols to resins. However, in the presence of a basic catalyst, we have been able to find no evidence of the formation of 2,2′-dihydroxydibenzyl ether ("salireton"), evidence that diphenylmethane links are formed directly. This confirms Ziegler and Lercher's statement[12] that heating saligenin yields this ether, and also confirms their observation that the ether is remarkably stable toward alkali (even boiling aqueous sodium hydroxide leaves it unaffected). Further to check this question, saligenin was heated at 98.5° until a substantial amount of the ether had been formed and then base was added. If the ether were an intermediate, the reaction rate should increase to some value greater than that normally observed for the catalyzed reaction, since the concentration of active intermediate would have been built up. Actually, the reaction rate after addition of the catalyst was somewhat lower than that normally observed. In other words, the ether present acted merely as a diluent. The anticipated change in order was also observed, the specific rate changing from 5.85×10^{-4} kg./mole/min. (2nd order) to 3.8×10^{-4}/min. (1st order).

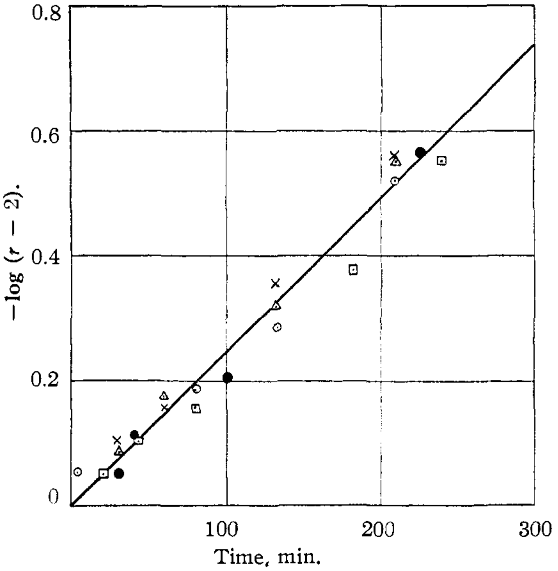

Fig. 5.—Effect of type and concentration of base on the self-condensation of saligenin: ●, run 78, 0.174 mole of T. E. A.; ○, run 58, 0.348 mole of T. E. A.; □, run 59, 0.696 mole of T. E. A.; ×, run 66, 0.174 mole of sodium hydroxide; △, run 67, 0.174 mole of quaternary ammonium base.

A clear explanation for the change in reaction order on adding alkali to saligenin cannot be developed from the data thus far obtained. It seems reasonable, however, that one or more equilibrium steps involving saligenin and basic catalyst, followed by a final irreversible step akin to cationoid attack upon the phenolic nucleus, should be considered. The apparent independence of rate with base concentration or basic strength is at present impossible to reconcile with any simple or obvious mechanism. Further information is needed for a satisfactory kinetic analysis of this phase of the problem.

Several runs involving saligenin and basic catalyst were carried considerably beyond the 50% reaction point (during which first order kinetics are valid). If only linear polymeric products are assumed to be formed under these conditions, the relationship between the average degree of condensation ($\bar{P}$) and the number of apparent reactive positions per mole of phenolic nucleus (r) is given by $\bar{P} = 2/(r - 1)$. It is then observed empirically that $\log \bar{P}$ is linear with t within experimental error, up to values of $\bar{P} = 8$ to 10. This useful result allows an estimate of degree of condensation to be made from bromination data.

Reaction of Saligenin with Phenol.—In absence of catalyst, saligenin and phenol, in equimolar proportions, react very slowly in a second order reaction; specific rate constant = 4.1×10^{-4} kg./mole/min. (Fig. 6). The product is presumably a mixture of isomeric dihydroxydiphenylmethanes, of which no single isomer

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(13) F. S. Granger, *Ind. Eng. Chem.*, **29**, 860 (1937).

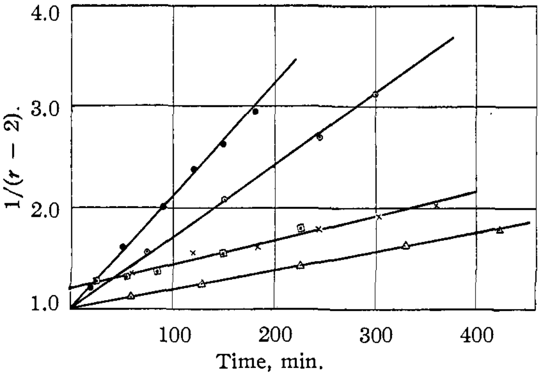

Fig. 6.—Reaction of saligenin with phenol in the presence of triethanolamine: □, *run* 45 at 99°; ×, run 15 at 99°; O, run 81 at 110.5°; ●, run 84 at 118°; in the absence of a catalyst, △, run 61.

could be isolated. In the presence of triethanolamine, the second order law is still obeyed well beyond the point of 50% disappearance of saligenin and at temperatures between 99 and 118°.

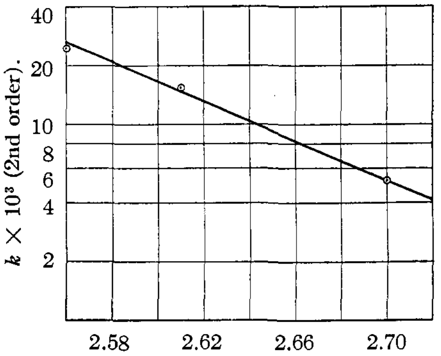

Fig. 7.—Arrhenius plot for the saligenin–phenol reaction in the presence of base.

The activation energy, *ca.* 31,500 cal./mole (from Fig. 7) is appreciably larger than that for the self-condensation of saligenin. When reacting in the proportion 1 saligenin:2 phenol, reasonable agreement with a second order rate law is still obtained, as shown in Fig. 8, where a conventional plot of $-\log\frac{b}{a}\left(\frac{a-x}{b-x}\right)$ against time is shown. By consideration of the reactivity toward bromine of the reactants and product (dihydroxydiphenylmethane) it is possible to put $(3r - 7)/(3r - 5)$ in place of $(a - x)/(2a - x)$.

Saligenin reacts faster with itself than it does with phenol. However, if the phenol were serving merely as diluent, adding catalyst should change the order of the reaction, as in the presence of pinacol; but this does not happen since the reaction of saligenin and phenol is second order in all cases. Catalyst exerts relatively little effect on the rate. Further, doubling the concentration of phenol does not double the rate—the reaction is actually slower under these circumstances. This discrepancy is occasioned either by a medium effect (which in this non-aqueous system is of unknown magnitude) or the phenol can be considered as playing a dual role, serving both as a reactant and as diluent.

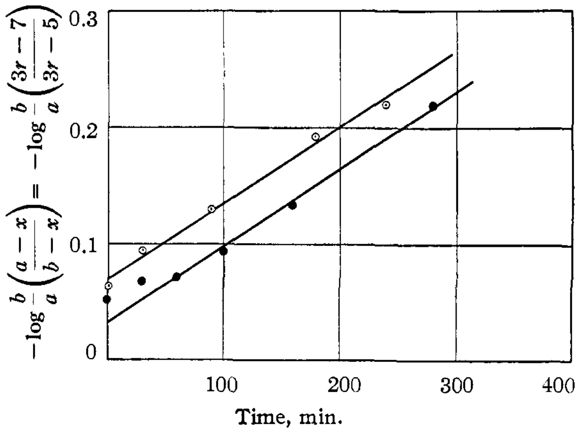

Fig. 8.—The reaction of saligenin + 2 phenol at 99°: runs 20 (O) and 46 (●).

Reaction of Saligenin with Resorcinol.—The reaction of saligenin with resorcinol is second order under any of the conditions investigated: namely, no catalyst or diluent present, diluent but no catalyst present, and diluent and catalyst both present. The product in each case is a trihydroxydiphenylmethane, probably the 2,4,2′-isomer. This substance was isolated in good yield from both catalyzed and uncatalyzed reactions. The best samples were purified by several recrystallizations from ethylene dichloride; m. p. 203.5–204.5°.

Anal. Calcd. for 2,4,2′-trihydroxydiphenylmethane ($C_{13}H_{11}O_3$): C, 72.2; H, 5.6; mol. wt., 216; hydroxyl equiv., 72.1. Found: C, 71.3; H, 5.6; mol. wt. (in camphor), 209; hydroxyl equiv., 71.1. The specific rate constant for the uncatalyzed, undiluted reaction is 3.28×10^{-3} kg./mole/min. (Fig. 9) only about eight times greater than that for the reaction of saligenin with phenol at the same temperature. The rate of reaction of saligenin with resorcinol, rather surprisingly, is only about twice that of the self-condensation of saligenin. The addition of triethanolamine has practically no effect upon this reaction (in pinacol). In presence of two moles of pinacol per mole of reactant the observed rate (1.06×10^{-3} kg./mole/min.) is about one third that observed in absence of diluent. In pinacol also when the molar ratio of reactants is 1:2 or 2:1 (Fig. 10), the specific rate constant, within experimental error, in either case is double that found for the equimolar reaction, indicating normal first power dependence of the rate upon the concentration of either reactant.

Acknowledgment.—The authors wish to thank Mrs. Mary Caldwell Chandler for the carbon and hydrogen analyses.

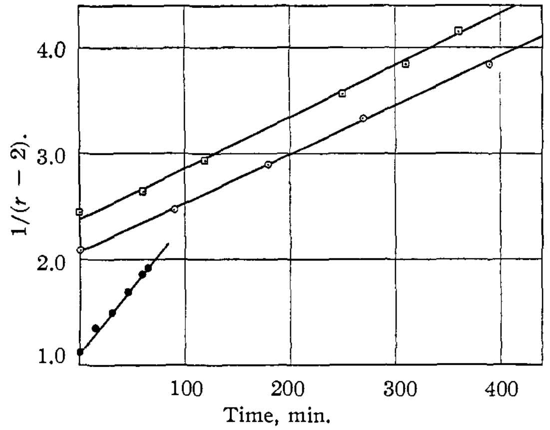

Fig. 9.—Reaction of saligenin with resorcinol at 99°: ●, run 10, 1 saligenin:1 resorcinol, no catalyst; ⊙, run 17, 1 saligenin:1 resorcinol:2 pinacol, no catalyst; ⊡, run 18, 1 saligenin:1 resorcinol:2 pinacol in the presence of triethanolamine.

Summary

1. The condensation reactions of *o*-methylol phenol (saligenin) with itself, with phenol and with resorcinol have been studied in presence and absence of basic catalysts.

2. In absence of catalyst, 2,2′-dihydroxydibenzyl ether is formed from saligenin in high yield by an apparently second order reaction and with an activation energy of 20,000 cal./mole.

3. In presence of triethanolamine, sodium hydroxide, or a quaternary ammonium base, the self-condensation of saligenin obeys first order kinetics during about the first 50% of potential reactivity, after which departure from this relationship is observed. The final product is a resinous solid. The activation energy is 18,500 cal./mole. The specific rate constant is independent of basic strength or base concentration within the range studied.

4. The relationships of (2) and (3) are essentially unaltered when pinacol is used as diluent.

5. The reactions of saligenin with phenol and resorcinol are second order both in presence or absence of base or diluent. With resorcinol, the major product is a crystalline trihydroxydiphenylmethane. Weakly basic catalyst has no appreciable effect upon the reaction velocity.

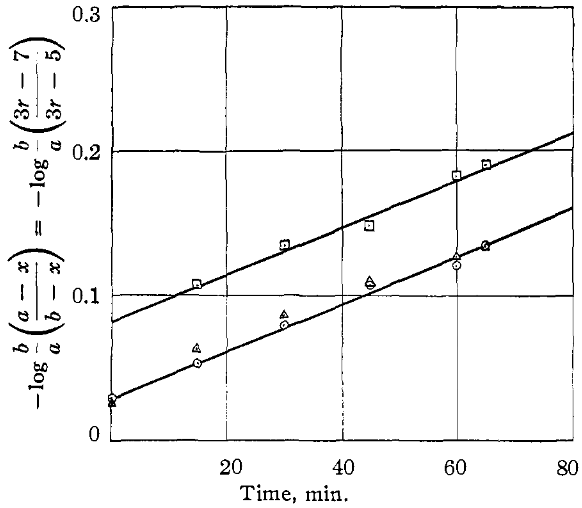

Fig. 10.—The reaction of saligenin with resorcinol at 99° and no catalyst: □, run 19, 1 saligenin:2 resorcinol:2 pinacol; O, run 21, 2 saligenin:1 resorcinol:2 pinacol; △, run 25, 1 saligenin:2 resorcinol:2 pinacol.

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The Acid-Catalyzed Decarboxylation of Cinnamic Acids

BY WILLIAM S. JOHNSON AND WALTER E. HEINZ

The experiments recorded herewith demonstrate that the decarboxylation of certain cinnamic acid types is promoted by mineral acid and that the rate of reaction is an increasing function of the concentration of the calayst. It appears, therefore, that the rate is influenced by the interaction of the catalyst with the organic acid, a conclusion which has profound bearing on the mechanism of the reaction and is particularly significant in view of the current feeling[1] that this is not a common type of behavior.

Experimental

The studies were carried out with the acids I-VI which, except for the last, were prepared *via* the Reformatsky reaction, followed by dehydration with formic acid and saponification according to general directions described elsewhere.[2] The decarboxylations were performed simply by boiling a solution of the organic acid in a mixture of 48% hydrobromic acid, acetic acid and water, the rate of reaction being determined by measurement of the volume of evolved carbon dioxide at appropriate intervals. The composition of the reagents (A–F) of various acid strength which were employed are given in Table I with the experimental data for calculation of the concentration of hydrobromic acid by volume. The description of the materials, apparatus and experimental procedure follows.

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[1] *Cf.* (a) Schenkel and Klein, *Helv. Chim. Acta*, **28**, 1211 (1945); (b) Schenkel, *ibid.*, **29**, 436 (1946); (c) Shenkel and Shenkel-Rudin, *ibid.*, **31**, 514 (1948).

[2] Johnson and Glenn, THIS JOURNAL, **71**, 1087 (1949).