sible explanation of this interaction would be the formation of hydrogen bonds, the hydrogen of the NH aniline group forming a bond between the nitrogen of this group and the oxygen of the CO group. Likewise, the pronounced changes in the NH aniline band in the aniline–isopropyl ether mixtures and the aniline–methyl cyanide mixtures suggest the association of these liquids through the formation of hydrogen bonds. There seems to be no interaction between the NH aniline group and carbon tetrachloride.

The apparent changes in the polarization of molecules in liquid mixtures as determined by dielectric constant measurements are no doubt in many cases due to changes in the electric moments of certain groups resulting from association of the liquids through the interaction of the dipoles of these groups. It should be possible through infra-red absorption measurements to ascertain in many of these mixtures which dipoles undergo pronounced changes and thereby to determine something of the nature of the linkage. The work is being continued on other mixtures in which the formation of hydrogen bonds may be anticipated. Preliminary results,[9] similar to those given above for aniline mixtures, indicate that water and also alcohols associate with certain other liquids through the formation of hydrogen bonds.

The writer wishes to thank Dr. E. K. Plyler for the use of his instrument and Dr. B. G. Carson, of Carson-Newman College, for his helpful discussions.

Summary

In mixtures of aniline with acetone, ethyl acetate, ethyl formate, methyl cyanide and isopropyl ether, the NH vibrational band of aniline is shifted to shorter wave lengths and its intensity is increased. In mixtures of aniline with carbon tetrachloride this band appears to remain constant. Other aniline bands remain approximately constant for all the mixtures. The CO band of acetone, ethyl acetate and ethyl formate is shifted to longer wave lengths, and its intensity increased in mixtures of these liquids with aniline.

It is suggested that the observed changes in the spectrum indicate association of the liquids through dipole interaction. The formation of hydrogen bonds is proposed as a possible interpretation of the results.

BELTON, TEXAS RECEIVED OCTOBER 26, 1936

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[9] Unpublished data obtained by the author.

[CONTRIBUTION NO. 174 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & CO.]

Kinetics of Condensation Polymerization; the Reaction of Ethylene Glycol with Succinic Acid

BY PAUL J. FLORY

Bifunctional condensation polymerizations, such as the formation of polyesters either from hydroxy acids or from glycols and dibasic acids,[1] proceed through the intermolecular reaction of the functional groups attached to bifunctional reactants. The reaction involved is fundamentally no different than the reaction between monofunctional reactants bearing the same functional groups; *e. g.*, in polyester formation the reaction is simply esterification, as Kienle and Hovey[2,3] have shown. Unless the reaction of one functional group of a bifunctional reactant changes the reactivity of the other group, all functional groups may be assumed to be equally reactive. When this is true, the reaction should be of the same kinetic character as the analogous monofunctional reaction. Unpublished experiments carried out in this Laboratory verify this deduction.

Recently Dostal and Raff[4,5] have examined the course of the reaction of ethylene glycol with succinic acid. They combined equimolar quantities either in dioxane solution or in the absence of solvent, and in two sets of experiments the succinic acid was dissolved in a large excess of glycol. The progress of the reaction was followed by titration of the unreacted acid in samples heated for various lengths of time at constant temperatures.

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[1] Carothers, *Chem. Rev.*, **8**, 359 (1931).

[2] Kienle and Hovey, THIS JOURNAL, **52**, 3636 (1930).

[3] Kienle and Hovey, *ibid.*, **51**, 509 (1929).

[4] Dostal and Raff, *Monatsh.*, **68**, 188 (1936).

[5] Dostal and Raff, *ibid.*, **68**, 117 (1936).

Inasmuch as the reaction takes place between two functional groups, Dostal and Raff assume that it is second order. As proof of this they cite the observation that the rate, expressed as the fraction reacting per unit time, increases as the square of the initial concentration when equivalents of the reactants are used. But this observation is actually indicative of a third order mechanism.

In the estimation of approximate activation energies Dostal and Raff use the quantity nE for the critical energy increment in the Arrhenius equation[6] where n is a factor (> 1) depending upon the average degree of polymerization, $\bar{x}$, of the polymer molecules. However, the polymer molecules are not formed through the *simultaneous* formation of several linkages between segments as this expression for activation energy implies, but through the *stepwise* formation of $\bar{x} - 1$ linkages between the $\bar{x}$ segments. The temperature coefficient is simply dependent upon the activation energy E required for one elementary reaction, and so n must equal unity regardless of $\bar{x}$. In view of the confusion in Dostal and Raff's discussion of their results, a re-interpretation seemed desirable.

To this end, for each temperature and concentration at which Dostal and Raff have furnished adequate data, their results have been compared by conventional graphical methods with both bimolecular and trimolecular kinetic equations. When equivalents of the reactants are used the bimolecular equation may be written in the form

$$C_0k_2t = 1/(1 - p) - 1 \qquad (1)$$

where C_0 is the initial concentration in *equivalents* of OH or of COOH groups per liter (Dostal and Raff use *moles* of reactant per liter), k_2 is the velocity constant in liters per equivalent per hour, t is the time in hours, and p is the extent of reaction, *i. e.*, the fraction of the COOH groups which has reacted at time t. For the trimolecular equation

$$2C_0^2k_3t = 1/(1 - p)^2 - 1 \qquad (2)$$

where k_3 is in (liters per equivalent)^2 per hour. When succinic acid was dissolved in a large excess of ethylene glycol, the concentration of the latter remained practically unchanged during the reaction. If the rate is dependent upon the first power of the acid concentration

$$C_gk_2t = -\ln(1 - p) \qquad (3)$$

where C_g is the concentration of glycol. If the rate is proportional to the second power of the acid concentration

$$C_gC_0k_3t = 1/(1 - p) - 1 \qquad (4)$$

where C_0 is the initial concentration of succinic acid.

Although the experimental error in Dostal and Raff's results is rather large, in most cases the reaction was carried far enough to justify a significant choice between the bimolecular (equations (1) or (3)) and trimolecular equations ((2) or (4)). For the reaction of equivalents of acid and glycol, plots of $1/(1 - p)^2$ *vs.* t are invariably more nearly linear than plots of $1/(1 - p)$ *vs.* t. For the reaction of succinic acid dissolved in a large excess of glycol $1/(1 - p)$, but not $\ln(1 - p)$, is approximately linear with t. To illustrate the accordance of the results with equation (2), the bimolecular and trimolecular velocity constants, calculated from equations (1) and (2), respectively, for the reaction of equivalents in the absence of solvent at 123° are given in Table I. It is apparent that k_3 is approximately constant, whereas k_2 decreases as the reaction progresses. Similarly in Table II, k_3 calculated from (4) for the reaction of succinic acid in an excess of glycol is more nearly constant than k_2 calculated from (3).

TABLE I

SECOND AND THIRD ORDER VELOCITY CONSTANTS FOR THE REACTION OF EQUIVALENTS OF ETHYLENE GLYCOL AND SUCCINIC ACID WITHOUT SOLVENT[a]

$T = 123$°C. $C_0 = 13$ equiv./liter

t, hours	$1 - p$	$k_2 \times 10^2$, l./equiv./hr.	$k_3 \times 10^2$, l.^{2}/equiv.^{2}/hr.
0	1.000		
.25	0.890	3.8	0.31
.5	.800	3.8	.33
1.0	.682	3.6	.34
2.0	.500	3.8	.44
4.0	.460	2.26	.276
5.0	.420	2.13	.276
6.0	.345	2.31	.365
10.0	.320	1.63	.260
19.0	.250	1.21	.233
24.0	.185	1.41	.347
28.0	.180	1.24	.315

[a] See Table 7 of ref. 4.

Graphically determined values of k_3 at various temperatures and concentrations are given in Table III. Examination of these velocity con-

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(6) Dostal and Raff equate p_2/p_1 (q_2/q_1 in their notation) to the Arrhenius factor $e^{-(nE/R)(1/T_2 - 1/T_1)}$ where p_1 and p_2 are, respectively, the extents of reaction at temperatures T_1 and T_2 during the times t_1 and t_2 for $t_1 = t_2$. This relationship can only be applied when the extent of reaction is very small. They should have equated t_1/t_2 for $p_1 = p_2$ to the Arrhenius factor.

TABLE II

SECOND AND THIRD ORDER VELOCITY CONSTANTS FOR THE REACTION OF SUCCINIC ACID IN AN EXCESS OF ETHYLENE GLYCOL[a]

$T = 131.5°$ $C_0 = 1$ equiv./liter $C_g = 30$ equiv./liter

t, hours	$1 - p$	$k_2 \times 10^2$, l./equiv./hr.	$k_3 \times 10^2$, l.²/equiv.²/hr.
0	1.000		
.25	0.852	2.14	2.31
.50	.783	1.63	1.85
.75	.735	1.37	1.60
1.00	.679	1.13	1.58
4.25	.380	0.76	1.28
8.00	.214	.64	1.53
14.00	.077	.61	2.86
18.00	.080	.47	2.13
24.00	.070	.37	1.85

[a] See Table II of ref. 5.

TABLE III

VELOCITY CONSTANTS

Source of data Ref.	Table	T., °C.	C_0, equiv./liter[a]	$k_3 \times 10^2$, liter²/equiv.²/hr.
4	2	150	0.20	~4.5
4	4	150	.50	3.8
4	5	120	1.00	~0.34
4	6	140	1.00	1.65
4	7	123	No solvent[b]	0.30
5	I	131.5	No solvent[b]	.60
5	II	131.5	1.00 acid in glycol[c]	1.43
4	8	140	1.00 acid in glycol[c]	2.70
		1,4-Butylene glycol + succinic acid		
4	9	140	1.00	1.02

[a] Dostal and Raff give concentrations in moles/liter. Unless otherwise stated the solvent was dioxane. [b] Based on the densities of the reactants and assuming no contraction on mixing we take $C_0 = 13$ equiv./liter. [c] Similarly, $C_g = 30$ equiv./liter.

stants obtained over a wide range of concentrations reveals that at a given temperature k_3 is almost independent of the concentration, thus substantiating the choice of kinetic order. It is especially significant that k_3 at 120° at 1.00 equiv./liter is nearly the same as k_3 at 123° in the absence of solvent. It is true, however, that the velocity constants for the reaction of equivalents tend to increase slightly with dilution (*e. g.*, note the 150° k's at $C_0 = 0.20$ and at 0.50), and the velocity constants for the reaction in glycol are greater than those obtained using equivalents. This suggests that a small part of the reaction may be bimolecular. The rates of reaction of 1,4-butylene glycol and of ethylene glycol are comparable at $C_0 = 1.00$ and $T = 140°$.

This analysis shows, therefore, that the reaction of ethylene glycol with succinic acid cannot be bimolecular as Dostal and Raff have supposed; it is approximately trimolecular, the rate being proportional to the first power of the concentration of hydroxyl groups and to the square of the concentration of carboxyl groups.

These results are in harmony with the conclusions reached by Goldschmidt[7,8] from his extensive studies of esterifications, and confirmed by the more recent work of Hinshelwood and co-workers.[9,10] According to these conclusions the esterification reaction requires a hydrion catalyst in addition to a molecule of the alcohol and one of the acid. In the case of esterifications catalyzed by an added acid[7,10] (to which Goldschmidt devoted most of his attention) the hydrion is furnished by this acid. In the "uncatalyzed" reaction the hydrion is furnished by another molecule of the acid undergoing esterification,[8,9] and hence the reaction is trimolecular since two molecules of acid and one of alcohol are required in the formation of the reaction complex. Rolfe and Hinshelwood's observation that the esterification reaction is catalyzed by traces of substances yielding hydrions may explain the irreproducibility in Dostal and Raff's results.

The three energies of activation calculated from the velocity constants in Table III for the polyesterification in the absence of solvent, in dioxane, and in an excess of glycol, respectively, are all within 2 kcal. of 25 kcal. Rolfe and Hinshelwood[9] find a much lower value, 13 kcal., for the reaction of methanol with acetic acid. For the second stage of the reaction of ethylene glycol with phthalic anhydride, *i. e.*, the reaction

$$\text{—O—C}_2\text{H}_4\text{—O—CO—C}_6\text{H}_4\text{—COOH} + \text{HO—C}_2\text{H}_4\text{—O—} \longrightarrow \text{—O—C}_2\text{H}_4\text{—O—CO—C}_6\text{H}_4\text{—CO—O—C}_2\text{H}_4\text{—O—} + \text{H}_2\text{O}$$

Kienle and Hovey[3] have obtained 22.6 kcal. for the activation energy, a value more nearly in agreement with the one for the reaction of glycol with succinic acid.

Polymerization Kinetics and Size Distributions

In a recent paper the author[11] has presented molecular size distribution equations for polymers formed by bifunctional condensations in which it is permissible to assume equal reactivity of all functional groups. By means of these equations the weight-fraction, mole-fraction, or number of any individual molecular species or group of mo-

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[7] Goldschmidt and co-workers, *Z. physik. Chem.*, **60**, 728 (1907); **70**, 627 (1910); **81**, 30 (1913).

[8] Goldschmidt, *Ber.*, **29**, 2208 (1896).

[9] Rolfe and Hinshelwood, *Trans. Faraday Soc.*, **30**, 935 (1934).

[10] Williamson and Hinshelwood, *ibid.*, **30**, 1145 (1934).

[11] Flory, THIS JOURNAL, **58**, 1877 (1936).

lecular species may be calculated. For polymers prepared from equivalents of the reactants the functions are entirely determined by the extent of reaction, p. When an excess of one reactant is used, the distribution functions are expressed as functions of both p and r, where r is the ratio of the initial concentration of the deficient group to the initial concentration of the group present in excess. No application of the equations to the kinetic problem of the relation of the amount of a particular species, or a particular group of species, to time of reaction was discussed. If the kinetic order of the reaction of the functional groups is known, such relationships can be derived by the following procedure. Considering, for example, the number of x-mer molecules N_x

$$\mathrm{d}N_x/\mathrm{d}t = (\partial N_x/\partial p)(\mathrm{d}p/\mathrm{d}t) \tag{5}$$

since $\mathrm{d}r/\mathrm{d}t = 0$. When $r \neq 1$ the form of the function N_x depends upon whether x is an even or an odd integer; when $r = 1$, $N_x = N_0p^{x-1}(1 - p)^2$ where N_0 is the initial concentration in numbers of molecules. $(\partial N_x/\partial p)$ will be a function of r and p when $r \neq 1$ and of p alone when $r = 1$. From the known kinetics of the process p and $\mathrm{d}p/\mathrm{d}t$ can be expressed as functions of t. Hence, $\mathrm{d}N_x/\mathrm{d}t$ can be expressed in terms of t, and integration will yield N_x as a function of t. In a similar way it is possible to relate the number of molecules within a particular group of sizes $y \leqq x \leqq z$ to time by replacing N_x by $\sum_{x=y}^{x=z} N_x$ in the above equations.

Dostal and Raff have attempted to utilize the size distribution equations in the interpretation of the kinetics of the glycol–succinic acid reaction.[12] Since the size distribution theory is based upon the assumption that the reaction consists of straightforward intermolecular reaction of functional groups, all of equal reactivity, it is obviously useless in an analysis of the kinetics of the reaction of the functional groups. Using the procedure outlined in the preceding paragraph and assuming that the reaction is second order, they have derived an equation for the relation of monomer concentration to time. They attempt to fit this equation in one case (Fig. 9 of ref. 4) to their experimental results which consist of measurements of concentration of COOH groups and not of monomer concentration. There is no foundation for this comparison.

Not having had access to the derivations of the size distribution equations at the time they carried out their work, Dostal and Raff presented the following arguments as proof that these equations are only approximate. First they compared the second order rate of disappearance of monomer given by $\mathrm{d}N_1/\mathrm{d}t = (\partial N_1/\partial p)(\mathrm{d}p/\mathrm{d}t)$ with the rate of disappearance of monomer given by the summation of the second order rates of reaction of monomer with each *other* molecular species, *i. e.*, with the summation $2k\sum_2^\infty N_1N_x$. $\partial N_1/\partial p$ and the concentrations, N_x, of each species were obtained from the distribution equations and substituted in each expression. The two expressions were compared and found to be somewhat different. In the above summation, however, they have omitted the term $2kN_1^2$, which arises from reaction of monomer with monomer. If this term is included, as it obviously should be, the two expressions are found to be identical. In a second similar attempt they have compared the second order rate of change in x-mer concentration given by $\mathrm{d}N_x/\mathrm{d}t = (\partial N_x/\partial p)(\mathrm{d}p/\mathrm{d}t)$ with the rate given by

$$k\sum_{y=1}^{y=x-1} N_yN_{x-y} - 2k\sum_{z \neq x} N_zN_x$$

In the second summation above the term $2kN_x^2$ should not have been excluded, for this term expresses the rate of disappearance of x-mer through reaction with another x-mer. The omission of this term caused Dostal and Raff to obtain nonidentical expressions.

As a result of these errors in setting up the summations, Dostal and Raff were led to the fallacious conclusion that the distribution equations are approximate in character. The distribution equations have been derived without introducing approximations beyond the basic assumption of equal reactivity of all functional groups.

Summary

Using the data of Dostal and Raff, it has been shown that the ethylene glycol–succinic acid polymerization is predominantly a trimolecular process. The rate of the reaction, which is simply an esterification, is proportional to the first power of the concentration of hydroxyl groups and to the square of the carboxyl group concentration. The activation energy for the reaction is about 25 kcal.

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(12) Dostal and Raff at the time they published their paper did not have at their disposal the complete account of the work on size distributions, but only a brief preliminary account included in a paper presented by Carothers [*Trans. Faraday Soc.*, **32**, 39 (1936)] before the Faraday Society, September, 1935.

A number of erroneous conclusions in Dostal and Raff's paper have been pointed out. The relation of the previously published molecular size distribution equations to kinetic problems has been discussed.

WILMINGTON, DEL. RECEIVED DECEMBER 21, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Organic Reactions with Boron Fluoride.[1] XIII. The Alkylation of Benzene with Alcohols

BY JAMES F. MCKENNA AND FRANK J. SOWA

Sulfuric acid[2] and aluminum chloride[3,4] have been used to accomplish the condensation of alcohols with benzene.

It was the purpose of this investigation to treat benzene with various alcohols in the presence of boron fluoride. An attempt was also made to determine the course of the reaction by subjecting primary, secondary and tertiary alcohols to the same treatment.

The reaction of alcohols with benzene might proceed by the direct elimination of water from the hydroxyl group of the alcohol and the hydrogen of the aromatic ring (see equation I below) or by first dehydrating the alcohol to an unsaturated compound with subsequent condensation into the aromatic nucleus (equations II and III).

$$CH_3(CH_2)_3\boxed{OH + H}C_6H_5 \longrightarrow CH_3(CH_2)_3C_6H_5 + H_2O \quad \mathrm{I}$$

$$CH_3CH_2CH_2CH_2OH \longrightarrow CH_3CH_2CH{=}CH_2 + H_2O \quad \mathrm{II}$$

$$CH_3CH_2CH{=}CH_2 + C_6H_6 \longrightarrow CH_3CH_2CH(CH_3)C_6H_5 \quad \mathrm{III}$$

Both *n*-propyl and isopropyl alcohols reacted with benzene to give identical alkylation products, namely: mono-, di-, and tri-isopropylbenzenes. Likewise *n*-butyl and *s*-butyl alcohol both yielded *s*-butylbenzene derivatives. Both isobutyl and *t*-butyl alcohols gave *t*-butylbenzene derivatives.

Since neither *n*-propyl, *n*-butyl nor isobutylbenzenes were isolated from the corresponding primary alcohols, the reaction did not take place to any appreciable extent according to equation (I). The direct elimination of water from the hydroxyl of the alcohol and the hydrogen of the aromatic nucleus therefore does not suggest itself as a plausible mechanism. On the other hand, however, the products of alkylation of benzene with alcohols all indicated that an unsaturated compound was first formed with subsequent condensation into the aromatic nucleus. It is, therefore, proposed that the mechanism of the reaction of benzene with an alcohol is first by dehydration to an unsaturated compound with subsequent condensation of the olefin with benzene according to equations (II) and (III).

Other alcohols besides the *n*-propyl, isopropyl, *n*-butyl, *s*-butyl and *t*-butyl were treated with benzene in the presence of boron fluoride. Cyclohexanol gave mono- and dicyclohexylbenzene; benzyl alcohol yielded mono- and dibenzylbenzene; allyl alcohol gave a small quantity of allylbenzene with a much larger quantity of light brown, high boiling material.

The disubstituted benzenes were the para derivatives with very small quantities of the ortho compounds. The positions were determined by oxidation. Sulfuric acid and boron fluoride both gave the para-substituted dialkylbenzene as the main product with a little ortho and no meta dialkylbenzene. When aluminum chloride is used, as an alkylation agent, in the Friedel–Crafts reaction, however, the main product is most often the meta dialkylbenzene.

The *t*-butyl, benzyl, cyclohexyl, allyl, *s*-butyl and isobutyl alcohols reacted very readily with benzene in the presence of boron fluoride while *n*-propyl and *n*-butyl reacted with more difficulty. Ethylene chlorohydrin reacted only very slightly to give a halogenated compound the structure of which was not determined. Phenol, as would be expected, did not react with benzene. Methyl and ethyl alcohols did not react under the conditions used in this investigation.

Experimental Part

Since the procedure was quite uniform for all of the reactions, only a general one will be described.

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[1] For previous paper see Sowa and Nieuwland, THIS JOURNAL, **58**, 271 (1936).

[2] Meyer and Bernhauer, *Monatsh.*, **53–54**, 721 (1929).

[3] Huston and Hsieh, THIS JOURNAL, **58**, 439 (1936).

[4] Tzukervanik, *J. Gen. Chem.* (*U. S. S. R.*), **5**, 117–120 (1935); *C. A.*, **29**, 4746 (1935).