[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

The Evaluation of Inductive and Resonance Effects on Reactivity. I. Hydrolysis Rates of Acetals of Non-conjugated Aldehydes and Ketones[1a]

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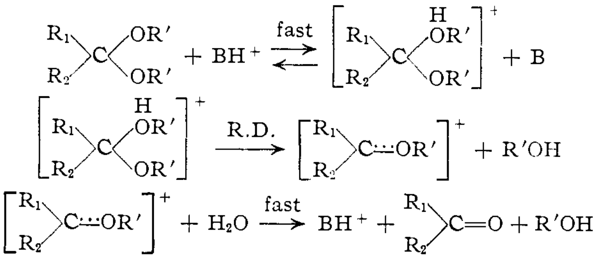
The second-order rate constants, *k*, for acid-catalyzed hydrolysis of twenty-four diethyl acetals and ketals, $R_1R_2C(OC_2H_5)_2$ have been determined in aq. dioxane at 25.0°. The constants for all of the acetals and ketals of non-conjugated aldehydes and ketones (except methyl neopentyl ketal) are correlated approximately by the equation: $\log(k/k_0) = (\Sigma\sigma^*)\rho^* + (\Delta n)h$. $\Sigma\sigma^*$ is the sum of the polar substituent constants for R_1 and R_2, previously determined by Taft (ref. 4) from ester hydrolysis rate data. ρ^* is a reaction series constant; Δn is the difference in the total number of α-hydrogen atoms in the groups R_1 and R_2 and the six in the standard of comparison, acetonal; *h* is an empirical constant measuring the facilitating effect of a single α-hydrogen atom on the rate. This equation may be interpreted as providing the first approximately quantitative evaluation of the hyperconjugation effects on rate in an aliphatic reaction series. An additive relationship between these effects and structure is found. The results further show that reactivity is correlated in an approximately quantitative manner by the assumption that the polar and hyperconjugation effects of substituents on rate are independent and separable variables.

The mechanism of the hydrolysis of acetals has been well investigated.[1b] All of the available facts are consistent with the following mechanism



According to this mechanism the empirical formula of the transition state differs from that of the ground state by an added proton.

The present investigation was undertaken with the thought that there might be a constant difference in the steric interactions of the substituents between the reactant and the transition states. If so, the rates in this reaction series would be substantially free of steric effects of substituent groups. These preliminary thoughts were supported by the work of Skrabal,[2] who had found that the effects of alkyl substituents on the rates of hydrolysis of acetals and ketals are additive. Steric effects on rate are not usually additive.[3,4] Skrabal's studies also included a rather limited series of formals, $CH_2(OR)_2$, in which structure is varied at the oxygen instead of the central carbon atom. Taft has correlated the hydrolysis rates for this series using eq. 1.

$$\log(k_1/k_0) = (\sigma^*)\rho^* \qquad (1)$$

The rate constant k_0 applies to the hydrolysis of dimethylformal (the standard of comparison) and the rate constant *k* applies to the hydrolysis of the general formal. σ^* is a constant characteristic of the group R and is a measure of the polar effect of the group. These constants were obtained by Taft from rate data for ester hydrolysis.[4] ρ^* is a parameter characteristic of the reaction series and is a measure of its relative susceptibility to the polar effects of substituents. Equation 1 expresses the approximate quantitative proportionality between the corresponding polar effects of substituents on rates and equilibria of various reaction series. The quantity $\sigma^*\rho^*$ is a measure of a polar effect even when other effects contribute to $\log(k/k_0)$.

Because other effects on reactivity are not, generally proportional to polar effects, eq. 1 will be obeyed only by those reaction series within which relative rates or equilibria are governed almost entirely by polar effects.[4]

The previously available data involve substituents of too narrow a range of polar and steric requirements to provide a convincing demonstration of the general applicability of eq. 1 to this type of reaction series. The present study was made to overcome this objection and to determine quantitatively, if possible, the effects contributing to reactivity in this series.

Results and Discussion

The rates of the acid-catalyzed hydrolysis of twenty-three diethyl acetals and ketals of the general formula $R_1R_2C(OC_2H_5)_2$ have been measured spectrophotometrically in 49.6% dioxane–50.4% water at 25°. Also the rate of hydrolysis of formal has been measured dilatometrically in the same solvent. The maximum effect of structure on rate amounts to nine powers of ten. The rate constants are summarized in Table I, along with other pertinent quantities.

Figure 1 shows a plot of $\log(k/k_0)$ *vs.* $\Sigma\sigma^*$, where *k* is the rate constant for the general acetal or ketal, $R_1R_2C(OC_2H_5)_2$, k_0 is the rate constant for acetonal, and $\Sigma\sigma^*$ is the sum of the σ^* values for R_1 and R_2. The plot reveals a linear dependence of $\log(k/k_0)$ on $\Sigma\sigma^*$ of satisfactory precision for all the monosubstituted acetals of unconjugated aldehydes (closed circles with tails in Fig. 1). In this series the slope of the correlation line, ρ^*, is -3.652 ± 0.081 and the intercept is -2.233, as determined by the method of least squares. A similar relation is found for the monosubstituted ketals of unconjugated ketones (open circles with tails in Fig. 1), excepting methyl neopentyl ketal. (This exception is discussed below.) For this series the slope, ρ^*, is

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[1] (a) The work herein reported was carried out on Project NR055–328 between the office of Naval Research and the Pennsylvania State University. Reproduction in whole or in part is permitted for any purpose of the United States Government. (b) *Cf.* references cited in earlier paper by M. M. Kreevoy and R. W. Taft, Jr., THIS JOURNAL, **77**, 3146 (1955).

[2] A. Skrabal, *Ber.*, **72B**, 446 (1939).

[3] R. W. Taft, Jr., THIS JOURNAL, **74**, 3120 (1952).

[4] R. W. Taft, Jr., *ibid.*, **75**, 4231 (1953).

TABLE I

RATES OF HYDROLYSIS OF ACETALS AND KETALS, $R_1R_2C(OC_2H_5)_2$, IN 49.6% DIOXANE–50.4% WATER AT 25.0°

No.	R_1	R_2	k_2, l. mole^{-1} sec.$^{-1}$	log (k/k_0)	$\left[\log\left(\frac{k}{k_0}\right) - 0.54\,(\Delta n)\right]$	$\Sigma\sigma^*$
1	CH_3	H	0.248	−3.482	−1.86	0.490
2	i-C_3H_7	H	0.164	−3.661	−0.96	0.290
3	t-C_4H_9	H	0.188	−3.602	−0.36	0.170
4	i-C_4H_9	H	0.167	−3.653	−1.49	0.365
5	$HOCH_2$	H	8.47×10^{-4}	−5.949	−3.79	1.045
6	C_2H_5	H	0.267	−3.449	−1.29	0.390
7	$C_6H_5CH_2$	H	8.70×10^{-3}	−4.936	−2.78	0.715
8	$ClCH_2$	H	1.03×10^{-5}	−7.863	−5.70	1.540
9	$(C_2H_5)_2CH$	H	0.312	−3.382	−0.68	0.265
10	$C_6H_5(CH_2)_2$	H	2.88×10^{-2}	−4.417	−2.26	0.570
11	H	H	4.13×10^{-5}	−7.260	−4.02	0.980
12	CH_3	CH_3	7.52×10^{2}	0.000	0.00	0.000
13	neo-C_5H_{11}	CH_3	9.2×10^{3}	1.086	+1.63	−0.140
14	C_2H_5	CH_3	7.2×10^{2}	−0.030	+0.51	−0.100
15	$C_6H_5CH{=}CH$	H	1.52×10^{2}	−0.695	+2.01	0.900
16	$ClCH_2$	CH_3	8.60×10^{-2}	−3.942	−3.40	1.050
17	$C_2H_5OCH_2$	H	8.62×10^{-4}	−5.940	−3.78	1.01[a]
18	$C_6H_5CH_2$	CH_3	8.45×10	−0.851	−0.31	0.225
19	$C_6H_5OCH_2$	CH_3	0.350	−3.333	−2.79	0.850
20	$HOCH_2$	CH_3	1.16×10	−1.812	−1.27	0.555
21	CH_3COOCH_2	CH_3	0.228	−3.578	−3.04	0.76[b]
22	$BrCH_2$	CH_3	0.138	−3.735	−3.20	1.030
23	C_6H_5	H	7.07	−2.030	+1.21	1.090
24	$CH_3CH{=}CH$	H	2.98×10^{2}	−0.401	+2.30	0.850

[a] Value for CH_3OCH_2 used for $CH_2CH_3OCH_2$. [b] Value for CH_3COOCH_2 given by 0.555 + 0.60/2.8.

−3.541 ± 0.176 and the intercept is −0.197.[5] Although the two lines have identical slopes within their precision they are widely separated and the points for other types of acetals and ketals scatter between and on both sides of these correlation lines.

Two facts immediately suggest that resonance effects rather than steric effects are primarily responsible for the lack of complete correlation of the data by eq. 1. First, acetals of α,β-unsaturated aldehydes shows a large deviation (*ca.* 5 log units) from the acetal line. Yet these unsaturated groups have small steric requirements in comparison to the $(C_2H_5)_2CH$ group, for example, which shows little deviation. A substantial resonance stabilization by α,β-unsaturated groups, however, is expected in a transition state having some oxocarbonium ion character. The latter condition is reasonable for the present reaction series in view of the postulated reaction mechanism. Second, trimethylacetal and formal deviate in the same direction and by an amount of the same order of magnitude. The t-butyl group and the hydrogen atom have very different steric requirements, but neither trimethyl acetal nor formal have α-hydrogen atoms available for hyperconjugation.

The conclusion that there are important resonance as well as polar effects on these hydrolysis rate constants is particularly well supported by the fact that the data for all the acetals and ketals of non-conjugated aldehydes or ketones (except that for the methyl neopentyl ketal) are satisfactorily correlated by eq. 2. This equation attributes the effect of structure on the free energy of activation to the sum of independent polar and hyperconjugation effects.

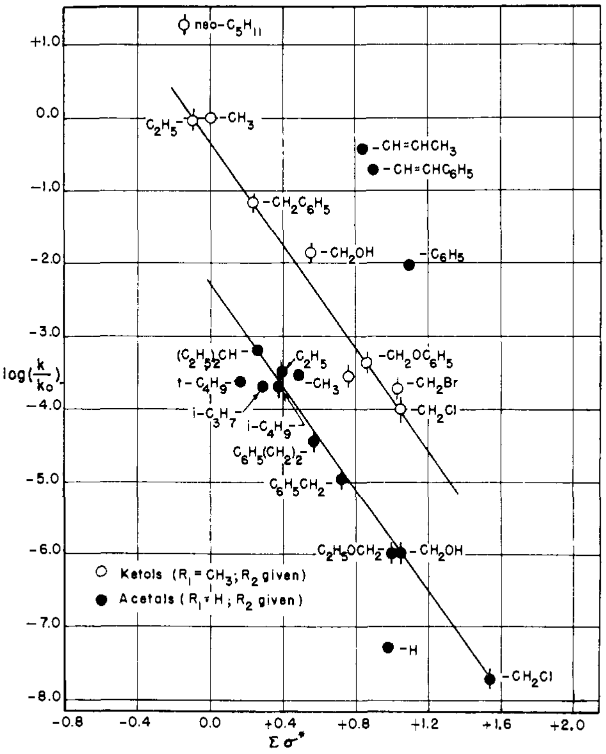

Fig. 1.—Plot of log (k/k_0) *vs.* $\Sigma\sigma^*$: Closed circles are acetals, $RCH(OC_2H_5)_2$. Open circles are ketals, $R(CH_3)$-$C(OC_2H_5)_2$. R is given with each point. For tailed points R = X–CH_2.

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[5] The data for methyl acetoxymethyl ketal were not used in obtaining these values because only a rough value of σ^* for the acetoxymethyl group is available. This ketal is included in the over-all correlation of eq. 2 discussed below, using a σ^* value of +0.76 for the acetoxymethyl group.

$$\log\left(\frac{k}{k_0}\right) = (\Sigma\sigma^*)\rho^* + (\Delta n)h \qquad (2)$$

In eq. 2, (Δn) is the difference between the number, n, of α-hydrogens atoms in R_1 and R_2 of the general acetal or ketal and the corresponding number of α-hydrogen atoms in the standard of comparison, acetonal, 6, *i.e.*, $\Delta n = n - 6$. The empirical constant h (0.54 ± 0.06) is attributable to the stabilization of the reaction transition state by a single α-hydrogen atom. The indicated value was obtained from all the data in a manner described in the Appendix. A reaction series constant, ρ^*, of -3.600 ± 0.115, the average of ρ^* values from eq. 1 for the monosubstituted acetal and ketal series, has been used in eq. 2. The correlation, shown in Fig. 2, covers twenty compounds having a total spread of nearly eight powers of ten in the rate constant k with a correlation coefficient of 0.986.[6] The probable error of a single point from the correlation line is 0.21 log unit.

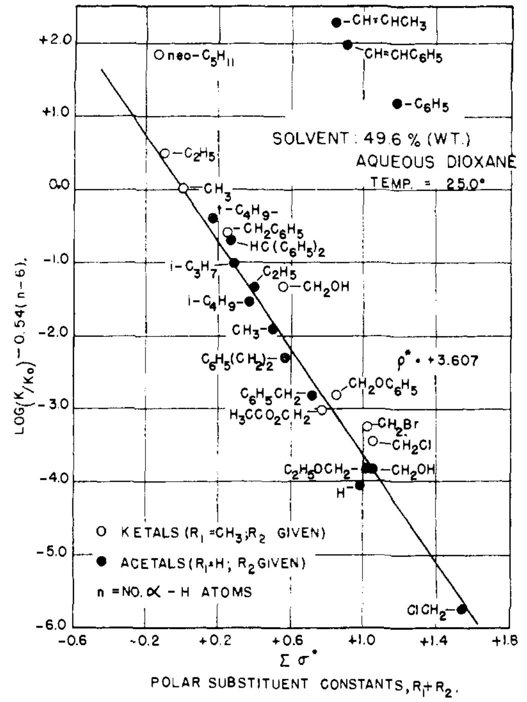

Fig. 2.—Plot of [log (k/k_0) − 0.54(Δn)] *vs.* $\Sigma\sigma^*$: Closed circles are acetals $RCH(OC_2H_5)_2$. Open circles are ketals $R(CH_3)C(OC_2H_5)_2$. R is given with each point.

Plotted as ordinate in Fig. 2 is the quantity [log (k/k_0) − $(\Delta n)h$], and as abscissa is $\Sigma\sigma^*$, the sum of the σ^* values for R_1 and R_2. Inasmuch as log (k/k_0) is a measure of the relative free energy of activation, the quantity [log (k/k_0) − $(\Delta n)h$] is presumed to measure only the contribution of the polar effects of R_1 and R_2 to the free energy of activation. That is, the corresponding measures of the contributions of hyperconjugation effects to the relative free energy of activation, $(\Delta n)h$, have been subtracted from the total free energy measures to obtain the polar effect measures. The linear polar energy relationship of Fig. 2 results.

The success of eq. 2 in correlating the hydrolysis rate constants provides strong argument that the following conditions apply, at least approximately, to reactivity in the present reaction series: (a) *Polar effects are proportional to the substituent constants, σ^*, and are additive;* (b) *Polar and C–H resonance effects are separate and independent variables;* (c) *Hyperconjugation effects are directly proportional to the number of α-hydrogen atoms;* (d) *Steric effects are second order in comparison to polar and resonance effects.*

Polar effects previously have been shown to be proportional to σ^* for a wide variety of reaction types.[4] The additive nature of polar effects has also been indicated, although somewhat less conclusively.[4] The present work strengthens the argument for the generality of both points (condition (a)).

The condition (b) that polar and resonance effects are independent variables has been suggested by ester hydrolysis rates.[3,7] The assumption that resonance effects are the same in the alkaline and the acid-catalyzed hydrolysis of ethyl benzoate permitted the assignment of a value of σ^* to the phenyl group.[3] This value is about 2.8 times the σ^* value for the $C_6H_5CH_2$ group and about 8 times that for the $C_6H_5CH_2CH_2$ group.[3,4] Since 2.8 has been generally accepted as the transmission coefficient for a saturated carbon atom[8] and has been found for other groups where the resonance complication does not occur,[3,4] the σ^* value obtained by Taft's method does not appear to be affected by the resonance (*ca.* 5 kcal./mole) which occurs in the ester between the phenyl and the carbethoxy groups.[3]

Eyring and Smith have suggested that the inductive effect of a substituent is dependent on the electron density at the functional center.[9] Their discussion suggests that a plot of rate constants *vs.* σ^* should give a curve rather than a straight line. Presumably it also implies a relation between $(\Delta n)h$ and $\rho^*(\Sigma\sigma^*)$. We find no fault with this argument, but the effects expected on this basis are not observed within the precision of eq. 2, in spite of the large variations in rate and structure. Indeed, the success which has attended the assumption that bond energies are additive[10] suggests that "saturation" and "feedback" effects[9] are so small that they will be difficult to detect in studies of relative rates.

The condition (c) that hyperconjugation effects are directly proportional to the number of α-hydrogen atoms is a new contribution. This condition, together with (b), is well supported by the present data. Thus eq. 2 holds with a single hyperconjugation parameter, h, for cases in which n, the number of α-hydrogens, varies from zero to six. This variation is accomplished by replacing α-hydrogen atoms by either strong electron withdrawing or releasing groups, *e.g.*, Cl or CH_3. That is, a single parameter suffices regardless of the intrinsic acidity of the α-hydrogen atom. Further an α-carbon atom with its substituents (α-hydrogen atoms or others) may be replaced by a single hydrogen atom. The results are summarized below in a man-

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[6] H. H. Jaffé, *Chem. Revs.*, **53**, 253 (1953).

[7] R. W. Taft, Jr., THIS JOURNAL, **75**, 4536 (1953).

[8] G. E. K. Branch and M. Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1941, p. 218.

[9] R. P. Smith and H. Eyring, THIS JOURNAL, **75**, 5183 (1953).

[10] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944, Chapter II.

ner which illustrates this point. Listed are the number of cases which follow eq. 2 for the various values of *n* together with the powers of ten in reactivity covered by the indicated series. If C–C hyperconjugation contributes to the hydrolysis rates the effects are apparently no larger than the precision of eq. (2).

n	2	5	Other
No. of cases	7	7	6[a]
Powers of 10 in reactivity	4.4	4.0	7.3

[a] Two have $n = 0$, two have $n = 1$, one has $n = 3$, and one has $n = 6$.

Condition (d) is probably the most limited of all those listed. The deviation of methyl neopentyl ketal from eqs. 1 and 2 probably represents a breakdown of this condition, *i.e.*, this may be a case in which the large steric requirements of the substituent groups increase reactivity.[11] Most of the scatter from eq. 2 (*cf.* Fig. 2) is also in the direction required by a steric acceleration. That is, points representing the bulkier ketals tend to fall above the correlation line while those representing smaller acetals fall below. This situation is under further investigation with other ketals having substituents of very large steric requirements.

Equation 2, of course, does not correlate the rate constants for the acetals of α,β-unsaturated aldehydes since it takes no account of conjugation. Conjugation effects on the hydrolysis rates will be discussed in detail in forthcoming papers. Table I and Figs. 1 and 2 show the behavior of this type of compound.

The large effect of substituents on hydrolysis rates found in the present work is in sharp contrast with the situation which prevails for the corresponding equilibrium.[12] No large effect on the equilibrium constant for the reaction was found by Hartung and Adkins for a series of saturated R groups of similar steric requirements.

$$RCHO + 2C_2H_5OH \rightleftharpoons RCH(OC_2H_5)_2 + H_2O$$

It is interesting to note that almost no effect of structure on reactivity would have been observed if the present study had been limited to alkyl substituted acetals. From the inception of the hyperconjugation concept, it has been suspected that the replacement of a single α-hydrogen atom by a methyl group will generally produce hyperconjugation and inductive effects on the rates of carbonium ion type reactions opposite in direction and similar in magnitude.[13] In the present reaction series the inductive effect of such a substitution increases the rate constant by 0.36 log unit while the accompanying hyperconjugation effect decreases it by 0.54 log unit. This approximate cancellation may be quite common and may account in part for the general failure to find a sharp dependence of rate on polar effects in aliphatic reactions series which include only alkyl substituents.[14]

Another interesting aspect of the present work is the failure to find evidence of neighboring group participation.[15] The magnitude of the conjugation and hyperconjugation effects indicates that the transition state has considerable carbonium ion character. Several of the substituents studied (*i.e.*, the phenyl group and the bromine atom) are known to be effective in neighboring group participation,[15,16] but acetals and ketals containing these groups are correlated by eq. 2 as well as the others. Possibly there are steric requirements for neighboring group participation that the present transition state cannot meet.[15b] In any event it is apparent that the susceptibility of a reaction transition state to neighboring group stabilization is a different function of structure than the susceptibility to stabilization by conjugation and hyperconjugation.

Experimental

Acetals and Ketals.—Acetals and ketals were, in general, made from ethyl alcohol, ethyl orthoformate and the corresponding carbonyl compound using a trace of mineral acid as a catalyst. Yields ranged from 30 to 80%. Exceptions are formal, acetal and chloroacetal, which were redistilled Eastman Kodak Co., white label products; hydroxyacetal, which was prepared from chloroacetal by the method of Beyerstedt and McElvain[17]; ethoxyacetal, which was made from bromoacetal and sodium ethoxide by the method of Späth[18]; and methyl hydroxymethyl ketal, which was made by hydrolyzing its acetate in aqueous base. With the exception of trimethylacetal, methyl neopentyl ketal and methyl phenoxymethyl ketal, for which analytical data are shown in Table II, these acetals and ketals are previously known compounds. Their boiling points and literature references are shown in Table III.

TABLE II

ANALYTICAL DATA FOR $R_1R_2C(OC_2H_5)_2$[a]

No.	R_1	R_2	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
3	*t*-C_4H_9	H	67.43	67.16	12.60	12.60
13	*neo*-C_5H_{11}	CH_3	70.15	70.54	12.85	12.94
19	$C_6H_5OCH_2$	CH_3	69.61	69.38	8.99	8.73

[a] Analyses were performed by Clark Microanalytical Laboratory, Urbana, Illinois.

Dioxane.—Dioxane was purified by the method of Vogel[19] and was freshly distilled from sodium before use, b.p. 99–100°, n^{25}_{D} 1.4227.

Kinetic Procedure.—All rates with the exception of that of formal were determined by following the appearance of the carbonyl peak in the ultraviolet with a Beckman D.U. spectrophotometer. The method has been previously described.[15]

The rate of hydrolysis of formal was measured dilatometrically in the usual way[20] in a dilatometer of conventional design and 500-ml. capacity. For these runs temperature was maintained constant ±0.002°. The reaction solutions contained 2% formal by volume.

A number of aldehydes, particularly those with electron withdrawing substituents, are in equilibrium with hydrates. Since the hydration reaction is relatively fast and reversible, the change in optical density or volume is directly proportional to the % reaction. Thus the hydrolysis rates can

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[11] (a) H. C. Brown, *Science*, **103**, 385 (1946); (b) H. C. Brown and R. S. Fletcher, THIS JOURNAL, **72**, 1223 (1950); (c) P. D. Bartlett, *Bull. soc. chim. France*, C100 (1951).

[12] W. H. Hartung and H. Adkins, *ibid.*, **49**, 2517 (1927).

[13] J. W. Baker, "Hyperconjugation," Oxford University Press, London, 1952, Chapter I.

[14] Statement attributed to H. C. Brown, *Chem. Eng. News*, **31**, 5058 (1953).

[15] (a) S. Winstein and E. Grunwald, THIS JOURNAL, **70**, 828 (1948); (b) M. Simonetta and S. Winstein, *ibid.*, **76**, 18 (1954). References to other papers on the same subject may be found in these papers.

[16] S. Winstein, C. R. Lindegren, H. Marchass and L. D. Ingraham, *ibid.*, **75**, 147 (1953).

[17] F. Beyerstedt and S. M. McElvain, *ibid.*, **58**, 529 (1936).

[18] E. Späth, *Monatsh.*, **36**, 4 (1915).

[19] A. I. Vogel, "Practical Organic Chemistry," Longmans Green and Co., New York, N. Y., 1948, p. 175.

[20] P. M. Leininger and M. Kilpatrick, THIS JOURNAL, **61**, 2510 (1939).

TABLE III

BOILING POINTS AND LITERATURE REFERENCES FOR $R_1R_2C(OC_2H_5)_2$

No.	R_1	R_2	B.p., °C.	Ref.
1	CH_3	H	102–104.5	*b*
2	*i*-C_3H_7	H	136–137	*c*
3	*t*-C_4H_9	H	146.6–146.8	
4	*i*-C_4H_9	H	155–159	*p*
5	$HOCH_2$	H	164–165	*d*
6	C_2H_5	H	123	*q*
7	$C_6H_5CH_2$	H	228–229	*e*
8	$ClCH_2$	H	155.5–157.5	*r*
9	$(C_2H_5)_2CH$	H	170–172	*f*
10	$C_6H_5(CH_2)_2$	H	120.5–122.5[t]	*g*
11	H	H	86	*h*
12	CH_3	CH_3	111–115	*i*
13	*neo*-C_5H_{11}	CH_3	177.5	
14	C_2H_5	CH_3	130–134	*j*
15	$C_6H_5CH{=}CH$	H	144[w]	*s*
16	$ClCH_2$	CH_3	155	*k*
17	$C_2H_5OCH_2$	CH_3	84[v]	*l*
18	$C_6H_5CH_2$	CH_3	245	*m*
19	$C_6H_5OCH_2$	CH_3	255	
20	$HOCH_2$	CH_3	83–84	*o*
21[a]	CH_3COOCH_2	CH_3	187	*o*
22	$BrCH_2$	CH_3	75.5[v]	*o*
23	C_6H_5	H	98[x]	*y*
24	$CH_3CH{=}CH$	H	148	*z*

[a] Saponification equivalent: calcd. 190, found 188. [b] H. Adkins and B. H. Nissin, "Org. Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 1. [c] M. S. Oeconomides, *Bull. soc. chem.*, [2] **35**, 500 (1881). [d] Ref. 9. [e] F. Sigmund and G. Marchart, *Monatsh.*, 48, 267 (1927). [f] R. I. Hoaglin and D. H. Hirsh, THIS JOURNAL, **71**, 3468 (1949). [g] F. Sigmund, *Monatsh.*, **53**, 607 (1929). [h] W. H. Greene, *Jahresberichte*, 491 (1879). [i] C. D. Hurd and M. A. Pollack, THIS JOURNAL, **60**, 1905 (1938). [j] H. E. Carswell and H. Adkins, *ibid.*, **50**, 235 (1928). [k] A. E. Arbusow, *Ber.*, **40**, 3304 (1907). [l] Ref. 10. [m] D. Shiho, *J. Chem. Soc., Japan*, **65**, 237 (1944). [o] W. W. Ewlampiew, *Ber.*, **62**, 2389 (1929). [p] C. R. Kinney and R. Adams, THIS JOURNAL, **59**, 897 (1937). [q] E. Fischer and G. Giebe, *Ber.*, **30**, 3054 (1897). [r] A. Kieben, *Ann.*, 104, 114 (1857). [s] T. Claisen, *Ber.*, **31**, 1016 (1898). [t] 9 mm. [v] 20 mm. [w] 17 mm. [x] 14 mm. [y] T. Claisen, *Ber.*, **40**, 3903 (1907). [z] S. M. McElvain, R. L. Clarke and G. D. Jones, THIS JOURNAL, **64**, 1966 (1942).

be obtained directly from the time change in optical density or volume of the system.[21] The reaction is essentially irreversible under the present conditions.[22]

Buffer solutions were used for acetonal, cinnamacetal, benzacetal, crotonacetal and the ketals of methyl benzyl, methyl neopentyl and methyl ethyl ketones because the hydrogen ion concentrations required for measurable rates with these compounds were too small to be reliably provided by strong acid solutions. The necessary ionization constants of the weak acids used were interpolated from the data cited by Harned and Owen.[23] The secondary salt effect was approximated by eqs. 3 and 4. Quantities in parentheses represent concentrations, $f_\pm$ is the mean ion activity coefficient for hydrogen ion and acetate ion, and Γ is the ional strength.[24]

$$(H^+) = \frac{K(HC_2H_3O_2)}{(C_2H_3O_2^-)f^2_\pm} \qquad (3)$$

$$-\log f_\pm = \frac{1.26\sqrt{\Gamma}}{1 + 2.0\sqrt{\Gamma}} \qquad (4)$$

The parameters used in eq. 4 are those required by theory.[25] The dielectric constant was interpolated from data cited by Harned and Owen[26] and the mean ionic radius (5.6 Å.) is that given by Harned.[27] Except for methyl neopentyl ketal, the second-order rate constants obtained in buffer solutions (like those in strong acid solutions) are directly proportional to the hydrogen ion concentration (*cf.* Table V). The second-order constants for methyl neopentyl ketal show a primary salt effect (*cf.* Table VI). The second-order rate constant given in Table I was therefore obtained by extrapolation to zero ional strength.

TABLE IV

HYDROLYSIS OF ISOBUTYRACETAL IN 49.6% DIOXANE–50.4% WATER IN 25.0°

$HClO_4$, *M*	10^4k_1, sec.$^{-1}$	10^2k_2, l. mole^{-1} sec.$^{-1}$
0.00677	11.1	16.4
.00677	10.7	15.8
.00271	4.45	16.4
.00271	4.45	16.4
.01355	21.8	16.1
.01355	22.8	16.8

TABLE V

HYDROLYSIS OF ACETONAL IN 49.6% DIOXANE–50.4% WATER AT 25.0°

Acetic acid, *M*	Acetate, *M*	10^4k_1, sec.$^{-1}$	$10^{-2}k_2$, l. mole^{-1} sec.$^{-1}$
0.00610	0.000853	18.0	7.62
.00610	.000853	17.3	7.34
.0305	.00426	21.6	7.26
.0305	.00426	21.7	7.30
.00482	.00213	6.23	7.42
.00482	.00213	6.57	7.82
.0241	.01065	8.85	7.64
.0241	.01065	9.01	7.79

With the exception of chloroacetal and formal the strong acid-catalyzed reactions follow a first-order rate law with very good precision (*ca.* 1%) within a given run. The second-order rate constants obtained from the first-order rate constants are reproducible within about 3%. The uncertainties in the second-order constants for chloroacetal and formal are 10%. Table IV demonstrates the second-order rate law for strong acid solutions. Table V shows the second-order rate law for a typical set of buffer solutions, while Table VI shows the hydrolysis rates for methyl neopentyl ketal.

Appendix

Assignment of Parameters.—In order to obtain the correlation of the data by eq. 2 using a single adjustable parameter, *h*, the value of ρ^* (+3.600 ± 0.115) was obtained by averaging the slopes of the monosubstituted acetal and monosubstituted ketal lines in Fig. 1. It was then assumed that the correlation line for Fig. 2 would pass through the acetonal point. This method permits the evaluation of the parameter, *h*, by eq. 5, and gives the value 0.54 ± 0.06.

$$h = \frac{\Sigma\left[\log\left(\frac{k}{k_0}\right) + 3.600\,(\Sigma\sigma^*)\right]}{\Sigma(\Delta n)} \qquad (5)$$

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(21) A. A. Frost and R. C. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 28.

(22) Hartung and Adkins, Ref. 6, found that the equilibrium constant for the reaction: $RCH = O + 2C_2H_5OH \rightleftarrows RCH(OC_2H_5)_2 + H_2O$ is always less than 0.15. This makes it very unlikely that more than 1.5% of any acetal remains unhydrolyzed at equilibrium.

(23) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 581.

(24) Ref. 23, glossary.

(25) Ref. 23, p. 39.

(26) Ref. 23, p. 118.

(27) H. S. Harned, *J. Phys. Chem.*, **43**, 275 (1938).

TABLE VI

HYDROLYSIS OF METHYL NEOPENTYL KETAL IN 49.6% DIOXANE–50.4% WATER AT 25.0°

Acetic acid, M	Acetate, M	10^4k_1, sec.$^{-1}$	$10^{-3}k_2$, l. mole^{-1} sec.$^{-1}$
0.00268	0.00426	46.7	17.8
.00268	.00426	50.2	19.2
.00268	.00246	51.8	19.8
.00268	.00426	50.7	19.3
.00243	.01438	24.7	26.5
.00243	.01438	23.5	25.3
.00243	.01438	23.2	25.0
.00243	.01438	21.7	23.3
.000486	.00287	10.6	16.2
.000486	.00287	10.1	15.5
.000481	.000360	44.3	10.8
.000481	.000360	44.7	10.9
.000481	.000360	44.5	10.8
.00804	.01278	85.0	25.2
.00804	.01278	83.3	24.7

The mean deviation, d, in h is obtained from eq. 6

$$d = \frac{\Sigma\left[\log\left(\frac{k}{k_0}\right) + 3.600(\Sigma\sigma^*) - 0.54(\Delta n)\right]}{\Sigma(\Delta n)} \qquad (6)$$

The validity of this procedure is supported by the fact that essentially the same value of h is obtained by the method least squares, using eq. 7

$$\log\left(\frac{k}{k_0}\right) + 3.600\,(\Sigma\sigma^*) = (\Delta n)h + a \qquad (7)$$

The deviation, a, of the acetonal point by this treatment is 0.12. However, the probable error of a single point obtained in this manner is not improved over the previous one.

A slightly better fit of the data can be obtained by using eq. 8

$$\log\left(\frac{k}{k_0}\right) = \rho^*(\Sigma\sigma^*) + (\Delta n)h + a \qquad (8)$$

Three parameters, ρ^*, h and a, are simultaneously adjusted to give the best fit for all the data.[28] Values of $\rho^* = -3.751 \pm 0.101$, $h = 0.606 \pm 0.033$ and $a = 0.354$ are obtained.

The probable error of a single point is reduced to ±0.186 log unit and the correlation coefficient is raised to 0.998. It can readily be seen that the values of ρ^* and h are the same, within the combined uncertainties, as those obtained by the first procedure. The slight improvement in the probable error of a single point, in the correlation coefficient, and in the probable error of ρ^* does not seem to justify the introduction of the parameter a, and the simultaneous adjustment of h and ρ^*.

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(28) (a) R. L. Anderson and T. A. Bancroft, "Basic Statistical Theory and Analysis of Experimental Models by Least Squares," McGraw-Hill Book Co., New York, N. Y., 1952, Chapter 14; (b) We are indebted to W. A. Pavelich for setting the generalized eqs. of ref. 28(a) in a form for convenient analysis of the data by eq. (6)—*cf.* Ph.D. thesis, W. A. Pavelich, Penn State University, June, 1955.

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The Synthesis of Long Chain α,ω-Dicarboxylic Acids

BY A. H. FRAZER AND J. C. SHIVERS

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A series of polymethyleneketo-α,ω-dicarboxylic acids and polymethylene-α,ω-dicarboxylic acids were prepared. The polymethyleneketo-α,ω-dicarboxylic acids were prepared from sebacyl chloride utilizing the ketene polymerization synthesis. The polymethylene-α,ω-dicarboxylic acids were prepared from the above keto acids by Clemmensen reduction. The properties of these acids are discussed.

The aliphatic long chain dicarboxylic acids of 600 to 3000 molecular weight have not been prepared previously. In general, the synthetic methods[1-5] used for preparing the shorter chain α,ω-dicarboxylic acids involved many steps and resulted in poor yields. Moreover, for the molecular weight range of 600 to 3000, the synthesis of intermediates involved would be extremely difficult, if not impossible.

This paper describes the synthesis of polymethyleneketo-α,ω-dicarboxylic acids and polymethylene-α,ω-dicarboxylic acids with average molecular weights in the 600 to 3000 range. The synthesis developed for the preparation of these products is an extension of work reported by Sauer[6-8] and Blomquist and co-workers.[9-11] Sauer has shown that a polymeric ketene was obtained on the dehydrohalogenation of sebacyl chloride. Blomquist and co-workers also report that a small amount of polymeric material was obtained in the synthesis of macrocyclic ketones *via* ketene dimer formation from sebacyl chloride and triethylamine in dilute solutions. The polymeric products were not fully characterized. In the synthesis described in this paper the polymeric diketenes (I) prepared from the acid chlorides of dibasic acids were hydrolyzed to the corresponding polymethyleneketo-α,ω-di-

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