and the N-methyl group. The rate of hydrolysis is expected to increase with increasing steric inhibition of resonance in the reactant state. Since the reactant state is common to both $k_2$ and $k_3$ and the resonance interaction with the carbonyl group may be expected to be lost in both "saturated" transition states, this steric effect should cancel in the $k_3/k_2$ ratio.

The proposed steric inhibition of resonance in the anilide is consistent with the fact that the second-order hydrolysis constant for trifluoro-N-methylacetanilide is twenty-five times greater than that for trifluoroacetanilide. The greater rate constant for the N-methylanilide cannot be attributed to the greater electron-releasing power of the methyl group or to "ordinary" steric hindrance to addition to the carbonyl reaction center. These factors are both expected to decrease instead of increase the rate.

It is of interest to consider the predictions of equation 6 with respect to the N-methylanilides of alkanecarboxylic acids. Considering as an example N-methylacetanilide, the adjusted $\sigma^*$ and $E_s$ values for the methyl group ($-0.490$ and $-1.24$, respectively) substituted in equation 6 give $k_3/k_2 = 0.06$. Thus at 1 *M* hydroxide concentration, while about 77% of the hydrolysis of N-methylformanilide occurs by the third-order process, it is predicted that only 5% of the N-methylacetanilide hydrolysis would be third-order. In 0.1 *M* NaOH, the figure expected for third-order hydrolysis of N-methylacetanilide is less than 1%. Since much of the previous work on the alkaline hydrolysis of anilides and amides has involved the derivatives of alkanecarboxylic acids, equation 6 suggests an explanation for the apparent inconsistency between the rate equations established in the present work and the "classical" second-order kinetics reported in the previous studies.

UNIVERSITY PARK, PENNA.

---

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

# The Evaluation of Inductive and Steric Effects on Reactivity. The Methoxide Ion-catalyzed Rates of Methanolysis of *l*-Menthyl Esters in Methanol[1]

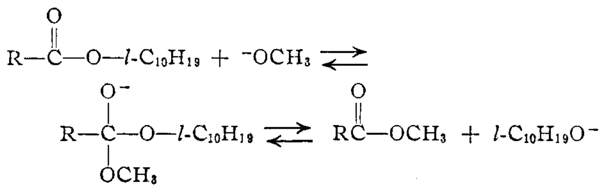
BY WILLIAM A. PAVELICH AND ROBERT W. TAFT, JR.

RECEIVED APRIL 8, 1957

The sodium methoxide-catalyzed rates of methanolysis of a series of *l*-menthyl esters of the general formula $RCO_2C_{10}H_{19}$ have been determined polarimetrically in methanol at 30°. The results indicate that the reaction takes place by the normal $B_{Ac}2$ mechanism. The substituents R have been varied over a wide range of polar and steric requirements leading to a spread of reactivities of six powers of ten. The effects of unconjugated ($\alpha,\beta$-saturated) substituents on the rate are correlated with acceptable precision by equation 1: $\log(k/k_0) = \sigma^*\rho^* + \delta E_s$. Evidence is thus provided that the effects of structure on the free energy of activation may be separated to the sum of independent polar and steric effects. The enthalpies and entropies of activation obtained for the formate, acetate, dichloroacetate and benzoate esters are discussed.

The present investigation has been carried out to provide further information on the mechanism and the effect of structure on the rates of base-catalyzed ester interchange. Despite the similarity in reactions, the kinetic evidence pertinent to ester interchange is far less extensive than that for the saponification of esters.

The sodium methoxide-catalyzed methanolysis of *o*-, *m*- and *p*-substituted *l*-menthyl benzoates in methanol has been shown to proceed by a mechanism analogous to that for normal ($B_{Ac}2$)[2] alkaline saponification[3]



$$R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}l\text{-}C_{10}H_{19} + {}^-OCH_3 \rightleftarrows$$

$$R{-}\underset{\underset{\displaystyle OCH_3}{|}}{\overset{\overset{\displaystyle O^-}{|}}{C}}{-}O{-}l\text{-}C_{10}H_{19} \rightleftarrows R\overset{\overset{\displaystyle O}{\|}}{C}{-}OCH_3 + l\text{-}C_{10}H_{19}O^-$$

$$l\text{-}C_{10}H_{19}O^- + CH_3OH \rightleftarrows CH_3O^- + l\text{-}C_{10}H_{19}OH$$

The reaction rates for *m*- and *p*-substituted benzoates follow the Hammett linear free energy relationship, $\log(k/k_0) = \sigma\rho$, with a reaction constant, $\rho$, essentially equal to that for the saponification of corresponding ethyl benzoates. The reaction rates for *o*-substituted benzoates show classical steric hindrance effects.

The rates of acid-catalyzed methanolysis, *n*-propanolysis and isopropanolysis of six $\beta$-naphthyl esters of alkane carboxylic acids parallel corresponding ester hydrolysis and carboxylic acid esterification rates.[4] The retarding effect of $\alpha,\beta$-unsaturated substituents in the acyl component on the rates of acid-catalyzed methanolysis of *l*-menthyl esters has been investigated.[5]

A study of the effect of structure on the position of equilibrium in the ester interchange reaction has shown only relatively minor effects, in contrast to the large effects found (in the present study, for example) in the reaction rates.[6]

In the present investigation the kinetics of the sodium methoxide ion-catalyzed methanolysis of twelve *l*-menthyl esters of the general formula, $RCO_2C_{10}H_{19}$ have been determined polarimetrically at 30.0°. The effect of structure of the group R on the reaction rates, which was of special interest,

---

[1] This work was supported in part by the Office of Naval Research, Project NR055-328. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 754.

[3] R. W. Taft, Jr., M. S. Newman and F. H. Verhoek, THIS JOURNAL, **72**, 4511 (1950).

[4] M. Harfenist and R. Baltzly, *ibid.*, **69**, 362 (1947).

[5] B. Dasannacharya, *ibid.*, **46**, 1627 (1924).

[6] P. R. Fehlandt and H. Adkins, *ibid.*, **57**, 193 (1935).

TABLE I

PHYSICAL PROPERTIES OF *l*-MENTHYL ESTERS, $RCO_2C_{10}H_{19}$

| R | Boiling points[a] Exptl. °C. | Mm. | Lit. °C. | Mm. | $n^{25}D$ Exptl. | $-[\alpha]^{25}D$ ($c$ 2–5)[b] Exptl. | Lit. | Ref. |
|---|---|---|---|---|---|---|---|---|
| H | 44 | 2 | 98 | 15 | 1.4476[j] | 83.3° | 79.5°,[i] 79.1° | c,d |
| | | | 219 | 730 | | | | |
| $CH_3$ | 153 | 85 | 108 | 15 | 1.4449 | 77.6 | 79.4[i] | c |
| $C_2H_5$ | 50 | 1 | 118 | 15 | 1.4462 | 80.6 | 75.5 | c |
| $ClCH_2$ | 61 | 1.5 | .. | .. | 1.4640 | 64.5 | 73.9 | e |
| $Cl_2CH$ | 87 | 1 | .. | .. | 1.4696 | 64.7 | 63.6 | e |
| $N\equiv CCH_2$ | 83–84[f] | | 83–84[f] | | .... | 83.7 | 80.7,[i] 81.2 | e,g |
| $n$-$C_5H_{11}$ | 198 | 85 | 153 | 15 | 1.4482 | 60.6 | 62.1 | c |
| $(CH_3)_3C$ | 67 | 1 | .. | .. | 1.4410 | 83.1 | .. | .. |
| $(CH_3)_3CCH_2$ | 79 | 1 | .. | .. | 1.4474 | 65.0 | .. | .. |
| $(CH_3)_3Si(CH_2)_2$ | 91 | 0.3 | .. | .. | 1.4537 | 61.3 | .. | .. |
| $C_6H_5OCH_2$ | 114 | 0.08 | .. | .. | 1.5020 | 55.6 | .. | .. |
| $CH_3CH{=}CH$ | 72 | 2 | 134 | 11 | 1.4662 | 85.5 | 91.6 | h |

[a] Mean value of b.p. given. Typical b.p. range 2°. [b] Exptl. values are given for solutions in absolute methanol. In most cases literature values are for the pure ester. [c] L. Tschugaeff, *Ber.*, **31**, 360 (1898). [d] R. N. Smith and W. V. Bolliger, *J. Chem. Ed.*, **27**, 369 (1950). [e] L. Tschugaeff, *J. russ. phys. chem. soc.*, **34**, 606 (1902). [f] Melting point. [g] D. A. Bowak and A. Lapworth, *J. Chem. Soc.*, **85**, 43 (1904). [h] H. Rupe, *Ann.*, **327**, 170 (1903); H. Rupe and E. Busolt, *ibid.*, **369**, 335 (1909). [i] At 20°. [j] Literature value 1.4480.

has been investigated extensively by the use of groups with widely varying polar, steric and resonance requirements. The results have been analyzed to provide a quantitative evaluation of the contributions of polar, steric and resonance effects to the free energy of activation. The energies and entropies of activation have been determined for the formate, acetate and dichloroacetate esters.

## Experimental

**Materials.**—*l*-Menthol was recrystallized from ethanol-water; $\alpha^{30}D$ −48.8°. Dry methanol was prepared by the method of Lund and Bjerrum[7] from the commercial product. Solutions of sodium methoxide in methanol were prepared by treating freshly cut sodium with dry methanol. The solutions were allowed to stand several days to allow the oxide to aggregate and were filtered under a nitrogen atmosphere through a filter-stick containing glass wool.

The esters used were prepared either by I, direct esterification of the carboxylic acid with *l*-menthol, or II, reaction of the acyl chloride with the alcohol. Method I was used to prepare the formate, cyanoacetate and β-trimethylsilylpropionate esters. Method II was used for the acetate, chloroacetate, dichloroacetate, propionate, 2,2-dimethylpropionate, 3,3-dimethylbutyrate, *n*-hexanoate, crotonate and phenoxyacetate esters.

Acids and acid chlorides were obtained from Eastman Kodak Co., except 3,3-dimethylbutyric acid, obtained from stock, and β-trimethylsilylpropionic acid, which was kindly provided by Dr. Leo H. Sommer. The materials were distilled prior to use. Physical properties of the esters are listed in Table I (b.p.'s and m.p.'s, uncor.). Table II gives analytical data.

TABLE II

ANALYTICAL DATA FOR *l*-MENTHYL ESTERS, $RCO_2C_{10}H_{19}$[a]

| R | Carbon, % Found | Calcd. | Hydrogen, % Found | Calcd. |
|---|---|---|---|---|
| $(CH_3)_3C$ | 74.67 | 74.95 | 11.66 | 11.74 |
| $(CH_3)_3CCH_2$ | 75.14 | 75.54 | 11.61 | 11.88 |
| $(CH_3)_3Si(CH_2)_2$ | 67.68 | 67.54 | 11.05 | 11.34 |
| $C_6H_5OCH_2$ | 75.05 | 74.44 | 9.09 | 9.02 |

[a] Analysis by G. Weiler and F. G. Strauss, Oxford, England, or Clark Microanalytical Laboratory, Urbana, Ill.

**Kinetic Procedure.**—Jacketed polarimeter tubes, 5 dcm. in length, as previously described, were used to follow the course of all reactions, except for slow reactions studied at 30.0°. The latter reactions were carried out in non-jacketed all-glass tubes of 2 or 2.5 dm. length. The tubes were kept in the reaction thermostat and removed only for the short period required to obtain polarimeter readings. Water from the thermostat was circulated through the polarimeter jacket while readings were made for the faster reactions.

Reaction mixtures were made up at room temperature in a manner similar to that described earlier[3] and transferred into a polarimeter tube placed in the thermostat. Temperatures of the reaction thermostat were maintained to ±0.01°, and it is estimated from several temperature determinations on the contents of the polarimeter tubes that the temperatures of solutions in the jacketed polarimeter tubes (standing in the polarimeter at room temperature) were maintained to ±0.1°.

Concentrations of ester for the 30° work were such as to give a total change in rotation of 2.5 to 4.0°. For experiments run at 15 and 45°, total changes in rotation were from 5.0 to 7.5°. All of the experiments at 15 and 45° were carried out in the jacketed 5-dcm. tubes.

Readings were determined over the course of 50 to 90% of complete reaction. Except for *l*-menthyl 2,2-dimethylpropionate, at least one experiment for each ester was allowed to go to completion. The final optical rotations generally agreed within 0.08° of that expected for *l*-menthol produced by complete methanolysis of the ester. For experiments at several representative concentrations of sodium methoxide, aliquots of the reaction mixture were titrated after ten half-times and found to agree within 1% of that expected for the standard base used to prepare to the reaction mixture.

Exceptions to these results were noted in several experiments for which the methoxide ion concentrations were less than $10^{-2}$ $M$. A loss of alkali was observed as well as incomplete conversion to *l*-menthol (final rotation differed as much as 1.5° from that expected). Apparently traces of water were introduced during the mixing of the solutions which led to ester saponification (undoubtedly of the resulting methyl ester) and loss of base. The extent of loss of base and the fraction of methanolysis completed before measurable departure from first-order kinetics was not reproducible for duplicate experiments. However, the second-order rate constants, $k_2$, obtained from the first half-time of all such experiments (using a calculated end-point) were reproducible. These results are in accord with the previously established fact[3] that the addition of water (even up to five molar) does not affect the initial rates of methanolysis of esters but does lead to a measurable loss of alkali during the later half-times of the reaction.

## Results

Pseudo first-order kinetics, $\ln(\alpha_\infty - \alpha) = -k_1t + \ln(\alpha_\infty - \alpha_0)$, are followed by each of the esters studied, in accord with the earlier work on methanolysis of benzoates.[3] At sodium methoxide concentrations below 0.3 $M$, the second-order rate

---

(7) H. Lund and J. Bjerrum, *Ber.*, **64**, 210 (1931).

law holds within the precision of the first-order constants as shown by the constancy of the ratio $k_1/(OCH_3) = k_2$ (Table III). At higher concentrations there is an indication of a positive salt effect, *i.e.*, the second-order constants trend upward. No attempt has been made to determine this salt effect quantitatively, instead most experiments were carried out at methoxide concentrations of less than 0.3 *M* in order to hold the salt effect to a minimum. The average deviation from the mean value of the second-order constants, $k_2$, given in Table IV is 2%.

TABLE III

TYPICAL RESULTS ILLUSTRATING SECOND-ORDER RATE EQUATIONS FOR THE METHOXIDE ION-CATALYZED METHANOLYSIS OF *l*-MENTHYL ESTERS

$RCO_2C_{10}H_{19}$ in Methanol at 30.0°

| R | Ester concn., mole-l.$^{-1}$ | $NaOCH_3$ concn., mole-l.$^{-1}$ | $10^4\ k$, sec.$^{-1}$ | $10^4\ k_2$, l.-mole$^{-1}$-sec.$^{-1}$ |
|---|---|---|---|---|
| $C_2H_5$ | 0.1359 | 0.0916 | 0.181 | 1.97 |
| | .1308 | .151 | .306 | 2.03 |
| | .1309 | .176 | .351 | 1.99 |
| | .1262 | .255 | .511 | 2.00 |
| | .1599 | .550 | 1.28 | 2.33 |
| $C_6H_5OCH_2$ | .351 | .00606 | 1.35 | $2.23 \times 10^2$ |
| | .309 | .0104 | 2.25 | $2.28 \times 10^2$ |
| | .283 | .0191 | 4.36 | $2.15 \times 10^2$ |
| $N{\equiv}CCH_2$ | .0788 | .00165 | 1.38 | $8.8 \times 10^2$ |
| | .0719 | .00274 | 2.63 | $9.6 \times 10^2$ |
| | .0845 | .0143 | 11.6 | $9.3 \times 10^2$ |
| $Cl_2CH$ | .0929 | .000783 | 5.25 | $6.71 \times 10^3$ |
| | .0809 | .00165 | 11.4 | $6.95 \times 10^3$ |

Temperature coefficients of rate were determined for the range 15-45° for the formate, acetate and dichloroacetate esters. Plots of log $k_2$ *vs.* $1/T$ are linear within the precision of rate constants. Table V lists enthalpies and entropies of activation and their precision measures obtained from the equations.[8]

The subscripts 1 and 2 refer to the lowest and highest temperature of the range covered, $r$ is the precision measure of the rate constant and $T$ is the mean temperature. Included in Table V are values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for the benzoate ester obtained from the data of the earlier work.[3]

## Discussion

The facts that the observed final rotation is that expected for complete conversion of ester to *l*-menthol and pseudo first-order kinetics are followed over the measurable course of the ester interchange reactions indicate that in each case the reaction takes place by the normal acyl–oxygen fission mechanism ($B_{Ac}2$).

TABLE IV

SECOND-ORDER RATE CONSTANTS (MEAN VALUES) FOR THE METHOXIDE ION-CATALYZED METHANOLYSIS OF *l*-MENTHYL ESTERS $RCO_2C_{10}H_{19}$ IN METHANOL ($\mu < 0.3\ M$)

| R | Temp., °C. | $10^4\ k_2$, l.-mole$^{-1}$-sec.$^{-1}$ |
|---|---|---|
| H | 15.8 | $1.41 \pm 0.06 \times 10^3$ |
| | 30.0 | $3.88 \pm .01 \times 10^3$ |
| | 44.2 | $9.70 \pm .03 \times 10^3$ |
| $CH_3$ | 15.0 | $1.66 \pm .03$ |
| | 30.0 | $5.81 \pm .25$ |
| | 45.0 | $1.92 \pm .04 \times 10$ |
| $Cl_2CH$ | 15.8 | $2.98 \pm .03 \times 10^3$ |
| | 30.0 | $6.83 \pm .12 \times 10^3$ |
| | 44.6 | $1.50 \pm .09 \times 10^4$ |
| $ClCH_2$ | 30.0 | $2.61 \pm .04 \times 10^3$ |
| $N{\equiv}CCH_2$ | 30.0 | $9.2 \pm .3 \times 10^2$ |
| $C_6H_5OCH_2$ | 30.0 | $2.22 \pm .05 \times 10^2$ |
| $C_2H_5$ | 30.0 | $2.00 \pm .02$ |
| *n*-$C_5H_{11}$ | 30.0 | 1.11 |
| $(CH_3)_3Si(CH_2)_2$ | 30.0 | $2.03 \pm 0.02$ |
| *t*-$C_4H_9CH_2$ | 30.0 | $1.3 \times 10^{-2}$ |
| $CH_3CH{=}CH$ | 30.0 | $9.7 \times 10^{-1}$ |
| *t*-$C_4H_9$ | 45.0 | $1.60 \times 10^{-2}$ |

The effects of structure in the acyl component on rate, as expected, are not correlated by a Hammett type linear free energy relationship[9] as shown in Fig. 1. Plotted as ordinate is log $(k/k_0)$ for the methanolysis rates at 30° and as abscissa log $(K/K_0)$ for the ionization constants of the corresponding carboxylic acid in water at 25°. The standard of comparison in each case (as in subsequent treatments of the relative rates) is the acetate derivative.

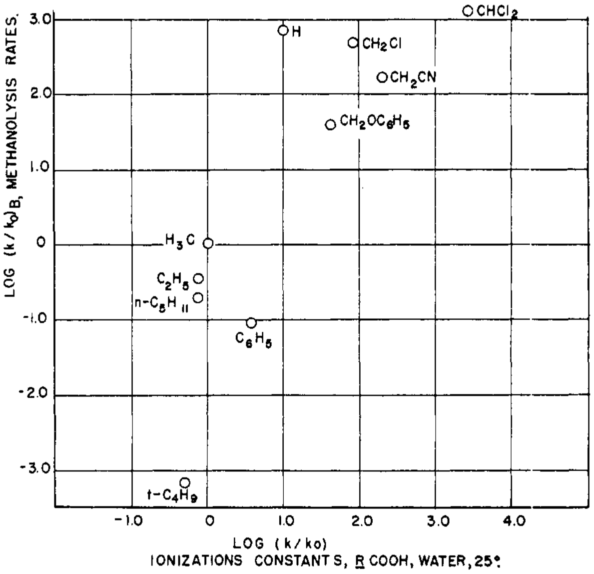


Fig. 1.—Failure of Hammett type relationship for base-catalyzed methanolysis of $RCO_2$-*l*-$C_{10}H_{19}$, methanol, 30.0°.

The structural effects on the methanolysis rates are similar to those in the rates of alkaline saponification of the corresponding esters as shown by the approximate linear free energy relationship of Fig. 2. This type of correlation has been formulated

---

(8) E. L. Purlee, R. W. Taft, Jr., and C. A. De Fazio, THIS JOURNAL, **77**, 837 (1955). The equation given in this reference for the enthalpy of activation and its precision measure is *incorrectly* transscribed in the last term with the ratios $r_2/k_1$ and $r_1/k_2$

$$\Delta H^{\ddagger} = \frac{RT_1T_2}{T_2 - T_1} \}\ln (k_2/k_1) \pm [(r_1/k_1)^2 + (r_2/k_2)^2]^{1/2}\} - RT$$

$$\Delta S^{\ddagger} = \frac{R}{T_2 - T_1} \{T_2 \ln k_2 - T_1 \ln k_1 \pm [(T_2\, r_2/k_2)^2 + (T_1\, r_1/k_1)^2]^{1/2}\} - R \ln (RT/Nh) - R$$

(9) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapt. VII.

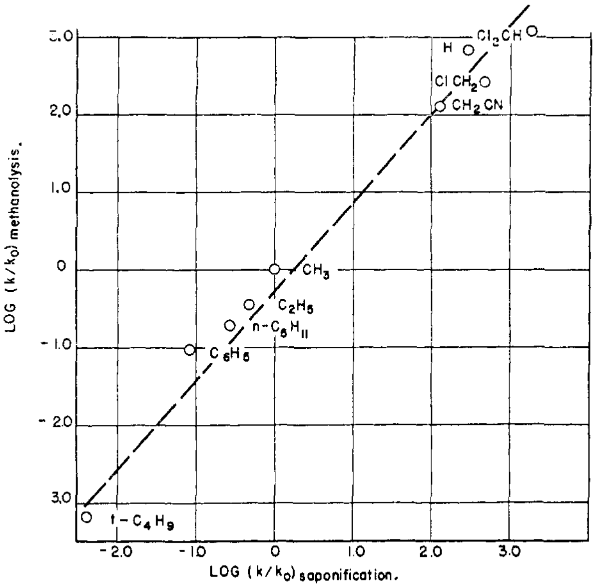


Fig. 2.—Correlation of rates of alkaline methanolysis of *l*-menthyl ester with rates of alkaline saponification of ethyl esters according to log $(k/k_0)_{\text{methanolysis}} = f \log (k/k_0)_{\text{saponification}}$.

by Taft by the relationship: $\log(k/k_0) = f(A)$, where $f$ is a reaction constant, and $A$ a substituent constant.[10]

However, the observed effects of unconjugated ($\alpha,\beta$-saturated) substituents on the methanolysis rates are more precisely correlated by the equation

$$\log(k/k_0) = \sigma^*\rho^* + \delta E_s \qquad (1)$$

$E_s$ and $\sigma^*$ are steric and polar substituent constants, respectively, obtained by Taft from rates of acid-catalyzed hydrolysis and alkaline saponification of esters.[11] The adjustable parameters, $\rho^*$ and $\delta$, are reaction constants measuring the susceptibility of the reaction series to polar and steric effects, respectively.

Using standard least squares methods for determining a bivariant regression plane[12] (*cf.* Appendix), it is found that the rates of methanolysis for all of the ten $\alpha,\beta$-saturated substituents investigated are satisfactorily fitted by equation 1, using the parameters: $\rho^* = 2.702 \pm 0.067$, $\delta = 1.301 \pm 0.055$, $\log k_0 = -3.299 \pm 0.064$. The probable error of a single point is 0.10 log unit for a range of reactivities of six powers of ten. The correlation coefficient is 0.996 (*cf.* Fig. 3).

Equation 1 was derived by Taft from correlation relationships (called linear polar and steric energy relationships) found to apply under limiting conditions of polar and steric effects, respectively.[11c] Basically, this equation attributes the effect of $\alpha,\beta$-saturated substituents on the free energy of activation to the sum of independent polar and steric effects. The polar effects quantitatively parallel corresponding $\sigma^*$ values (*i.e.*, $= \sigma^*\rho^*$) and the steric effects likewise follow corresponding $E_s$ values (*i.e.*, $= \delta E_s$). Values of $\sigma^*$ and $E_s$ and the $\log(k/k_0)$ values calculated by equation 1 are given in Table VI. It is apparent from the values of the substituent constants that the substituents selected for study have widely varying polar and steric requirements, *i.e.*, included are substituents for which $E_s$ values become increasingly more negative or positive with increasing $\sigma^*$ value. Thus the probability of a coincidental fit of the data to equation 1 is extremely low. The present data therefore constitute the first rigorous test of equation 1.

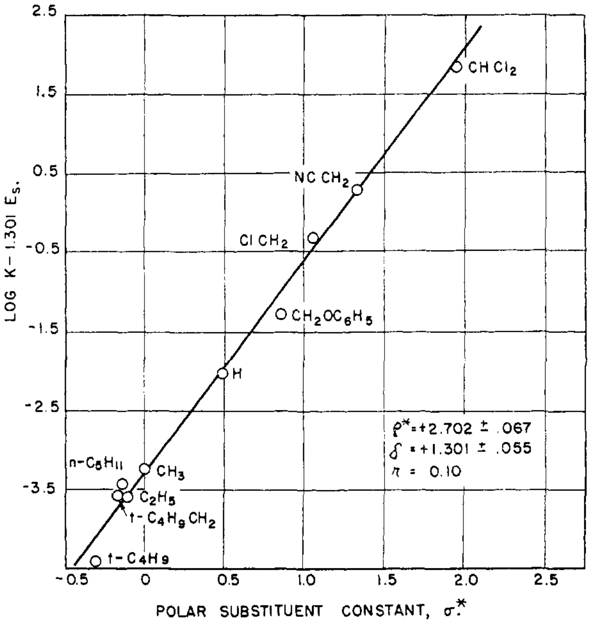


Fig. 3.—Correlation of rates of base-catalyzed methanolysis of *l*-menthyl esters, $RCO_2C_{10}H_{19}$, in methanol, 30.0°, according to the equation: $\log k - SE_s = \sigma^*\rho^* + \log k_0$.

TABLE V

ENTHALPIES AND ENTROPIES OF ACTIVATION FOR THE METHOXIDE ION-CATALYZED METHANOLYSIS OF *l*-MENTHYL ESTERS $RCO_2C_{10}H_{19}$ IN METHANOL

| R | $\Delta H^\ddagger$, kcal. | $\Delta S^\ddagger$, e.u. | $\Delta\Delta H^\ddagger$,[a] kcal. | $\Delta\Delta S^\ddagger$,[b] e.u. |
|---|---|---|---|---|
| $CH_3$ | $14.2 \pm 0.2$ | $-26.3 \pm 0.7$ | (0.0) | (0.0) |
| $Cl_2CH$ | $9.6 \pm .4$ | $-27.8 \pm 1.3$ | $-4.6 \pm 0.4$ | $-1.5 \pm 1.5$ |
| H | $11.8 \pm .3$ | $-21.6 \pm 0.9$ | $-2.4 \pm .4$ | $+4.7 \pm 1.4$ |
| $C_6H_5$ | $16.9 \pm .2$ | $-22.3 \pm 0.8$ | $+2.7 \pm .3$ | $+4.0 \pm 1.1$ |

[a] $\Delta\Delta H^\ddagger = \Delta H^\ddagger_{R} - \Delta H^\ddagger_{CH_3}$. [b] $\Delta\Delta S^\ddagger = \Delta S^\ddagger_{R} - \Delta S^\ddagger_{CH_3}$.

The possibility that the fit of the data to equation 1 is an accident of the two adjustable parameters, $\rho^*$ and $\delta$, is also rendered extremely low by independent evidence. The rates of methoxide ion-catalyzed methanolysis of *m*- and *p*-substituted benzoates under the same conditions as used in the present work (methanol, 30.0°) are correlated by the Hammett equation, $\log (k/k_0) = \sigma\rho$, with a value of $\rho$ of $+ 2.628$.[3,13] This value is the same within the combined precisions as the $\rho^*$ value obtained from equation 1. The equivalence of the

---

[10] R. W. Taft, Jr., THIS JOURNAL, **74**, 2729 (1952).

[11] R. W. Taft, Jr., *ibid.*, **74**, 3120 (1952); (b) **75**, 4231 (1953); (c) in M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapt. 13.

[12] R. L. Anderson and T. A. Bancroft, "Statistical Theory in Research," McGraw-Hill Book Co., Inc., New York, N. Y., 1952, Chapt. 14.

[13] H. H. Jaffé, *Chem. Revs.*, **53**, 202 (1953).

$\rho$ and $\rho^*$ values indicates that the presence of the second adjustable parameter, $\delta$, has no measurable effect on the value of $\rho^*$ obtained by best fit of the data to equation 1. The $\rho^*$ value for the ester interchange is also closely similar to that (2.48) for the alkaline saponification of ethyl esters of carboxylic acids and the $\rho$ value for the alkaline saponification of *m*- and *p*-substituted ethyl benzoates in aqueous acetone or ethanol.[14]

The larger $\delta$ value (1.301) for the ester interchange than for ester saponification (by definition, $\delta \equiv 1.000$) is quite reasonable. The increased susceptibility to steric effects is anticipated on the basis of the larger steric requirements of the alkyl component (*l*-menthyl for ester interchange and ethyl for ester saponification) and of the attacking reagent (methoxide ion and hydroxide ion, respectively). The $\delta$ value for the methanolysis of the *l*-menthyl esters appears to be quantitatively of the expected magnitude. The rates of the acid-catalyzed methanolysis of $\beta$-naphthyl esters of alkane carboxylic acids (which involve essentially no polar effects) have been correlated by a linear steric energy relationship with $\delta = 1.376$.[15]

Biechler and Taft have found that the second- and third-order alkaline hydrolysis rates of N-methylanilides do not fit equation 1 with acceptable precision, showing that reactivity in general is far too complex to be fitted coincidentally by this equation.[16] Pavelich and Taft have found that the benzenesulfonic acid-catalyzed rates of methanolysis of an extensive series of *l*-menthyl esters are correlated by equation 1 with similar precision to that reported in this paper for the methoxide ion-catalyzed rates.[17] Values of $\rho^*$ and $\delta$ are appreciably different for the acid-catalyzed reaction series (particularly the former). For both acidic and basic methanolysis rates the sign and magnitudes of $\rho^*$ and $\delta$ values provide further evidence of the normal acyl oxygen fission reaction mechanism.

The approximate linear free energy relationship between corresponding rates of methanolysis of the *l*-menthyl esters and rates of saponification of ethyl esters is expected in terms of equation 1 and the reaction constants. The values of $\rho^*$ and $\delta$ for the methanolysis reaction are 8 and 30% larger, respectively, than the corresponding reaction constants for saponification. Consequently, log $(k/k_0)$ values for the two reactions are roughly similar, or more exactly log $(k/k_0) \cong (+1.20)(A)$. This linear free energy relationship apparently is a coincidence of the similar values of $\rho^*$ and $\delta$ for these two reactions (that is, the linear free energy relationship is less fundamental than equation 1). Reaction series which are correlated by equation 1 with appreciably different $\rho^*$ and $\delta$ values (as, for example, the acidic and basic methanolysis rates) show no semblance of a linear free energy relationship.[17]

The rates of methanolysis of $\alpha,\beta$-unsaturated *l*-menthyl esters do not follow equation 1 but instead are appreciably slower than predicted. The deviations are quantitatively of the magnitude expected from the extra resonance stabilization in the unsaturated ester.[18] Resonance effects of $\alpha,\beta$-unsaturated substituents in rates of esterification and hydrolysis of esters have been discussed previously[11,18] and will be discussed in more detail for the methanolysis of *l*-menthyl esters in a subsequent paper.[17]

The enthalpies and entropies of activation given in Table V indicate that within the precision of measurement, the difference in the free energy of activation of the dichloroacetate and the acetate esters is equal to the difference in the enthalpy of activation, *i.e.*, the entropies of activation are equivalent. This result is consistent with the assignment of the effect of structure involved (−4.5 kcal./mole) as the resultant of opposed potential energy polar ($-2.303RT\sigma^*\rho^* = -7.2$ kcal.) and steric ($-2.303RTE_s\delta = +2.8$ kcal.) effects. Similarly, the difference in the free energy of activation of the benzoate and formate esters is equal within the precision of measurement, to the difference in the enthalpy of activation. This result is consistent with, and provides evidence for, the approximate assignment of the energy difference (+5.3 kcal./mole) to the potential energy of extra resonance stabilization of the benzoate ester.[11,18]

The substantially more positive entropy of activation of the formate relative to the acetate ester ($\Delta\Delta S^{\ddagger} = 4.7 \pm 1.4$ e.u.) is a result equivalent to that observed in a number of similar systems.[19] It is a result consistent with the idea that there is greater steric hindrance of internal molecular motions in the formation of the transition state for

TABLE VI

CORRELATION OF THE EFFECT OF STRUCTURE ON THE METHANOLYSIS RATES BY EQUATION 1

| R | $\sigma^*$ | $Es$ | log $(k/k_0)^{30.0°}$ exptl. | log $(k/k_0)^{30.0°}$ calcd. eq. 1 |
|---|---|---|---|---|
| $Cl_2CH$ | +1.940 | −1.54 | +3.07 | +3.18 |
| $N{\equiv}CCH_2$ | +1.300 | −0.94[b] | +2.20 | +2.21 |
| $ClCH_2$ | +1.050 | − .24 | +2.66 | +2.47 |
| $C_6H_5OCH_2$ | +0.850 | − .33 | +1.59 | +1.81 |
| H | + .490 | +1.24 | +2.83 | +2.87 |
| $CH_3$ | .000 | 0.00 | 0.00 | −0.06 |
| $(CH_3)_3Si(CH_2)_2$ | − .090[a] | − .12[c] | − .45 | − .46 |
| $C_2H_5$ | − .100 | − .07 | − .46 | − .42 |
| *n*-$C_5H_{11}$ | − .130 | − .40 | − .71 | − .93 |
| *t*-$C_4H_9CH_2$ | − .165 | −1.74 | −2.65 | −2.77 |
| *t*-$C_4H_9$ | − .300 | −1.54 | −3.08[d] | −2.87 |

[a] $\sigma^*$ obtained as 1/2.8($\sigma^*$) for $(CH_3)_3SiCH_2$ group. [b] $E_s$ obtained from the rate of acid-catalyzed hydrolysis of ethyl cyanoacetate in 70% (vol.) aq. acetone at 25.0° by the relationship, $E_s \equiv \log(k/k_0)$. The second-order rate constant for this reaction (using 0.05 *M* HCl) has been determined by Mr. Richard A. Javick as $5.14 = 10^{-6}$ l.-mole$^{-1}$-sec.$^{-1}$, employing a modified procedure of H. A. Smith and R. F. Myers (THIS JOURNAL, **64**, 2362 (1942)); 5-ml. aliquots were withdrawn from the reaction mixture and diluted with 20 ml. of $H_2O$ to effectively quench the reaction. The resulting solution was stirred rapidly and titrated slowly with standard base to avoid alkaline saponification of the unreacted ester. [c] $E_s$ obtained from the acid-catalyzed methanolysis rate of the *l*-menthyl ester, reference 17. [d] Temperature 45.0°. The value given is assumed to apply approximately at 30.0°.

---

[14] *Cf.* reference 11c, pp. 607, 649.

[15] R. W. Taft, Jr., THIS JOURNAL, **75**, 4538 (1953).

[16] S. S. Biechler and R. W. Taft, Jr., *ibid.*, **79**, 4927 (1957).

[17] W. A. Pavelich and R. W. Taft, Jr., unpublished results.

[18] M. M. Kreevoy and R. W. Taft, Jr., THIS JOURNAL, **79**, 4016 (1957).

[19] H. M. Humphreys and L. P. Hammett, *ibid.*, **78**, 521 (1956).

the acetate than that for the formate ester.[20] This result is also consistent with the structural effect on the entropy of solvation pictured by Humphreys and Hammett.[19] The possibility that the rate of methanolysis of the acetate is retarded relative to the formate by hyperconjugative stabilization in the ester[18] (as well as by the more electron-releasing inductive effect) is not eliminated, although perhaps it is rendered a less favored explanation by the observed difference in the entropies of activation.

The large negative entropies of activation observed in each case are consistent with the $B_{Ac}2$ mechanism, that is, are in accord with the entropy decrease expected for the addition of methoxide ion to the carbonyl group to form a transition state with a well-localized negative charge.

## Appendix

The following procedure was used to determine the best fit of the data to equation 1. The problem is to find the parameters for a plane whose general equation is

$$y = b_1x_1 + b_2x_2 + b_0 \tag{2}$$

The experimentally measured quantity is $y$, the variables are $x_1$ and $x_2$, and the correlation coefficients of these variables are $b_0$, $b_1$ and $b_2$. Following the method of "least squares" it is desired to find the values of $b_0$, $b_1$ and $b_2$ such that the sum of the squares of the vertical deviations of the measured values of $y$ ($n$ in number) from the regression plane are a minimum. The expressions for obtaining the correlation coefficients are given in terms of the quantities[21]

$$\begin{aligned}
C_{11} &= n\Sigma x_2^2 - (\Sigma x_2)^2 \\
C_{12} &= \Sigma x_1\Sigma x_2 - n\Sigma x_1x_2 \\
C_{13} &= \Sigma x_1x_2\Sigma x_2 - \Sigma x_1\Sigma x_2^2 \\
C_{22} &= n\Sigma x_1^2 - (\Sigma x_1)^2 \\
C_{23} &= \Sigma x_1\Sigma x_1x_2 - \Sigma x_1^2\Sigma x_2 \\
C_{33} &= \Sigma x_1^2\Sigma x_2^2 - (\Sigma x_1x_2)^2 \\
D &= C_{11}\Sigma x_1^2 + C_{12}\Sigma x_1x_2 + C_{13}\Sigma x_1
\end{aligned}$$

then

$$\begin{aligned}
b_1 &= \frac{1}{D}\left(C_{11}\Sigma x_1y + C_{12}\Sigma x_2y + C_{13}\Sigma y\right) \\
b_2 &= \frac{1}{D}\left(C_{12}\Sigma x_1y + C_{22}\Sigma x_2y + C_{23}\Sigma y\right) \\
b_0 &= \frac{1}{D}\left(C_{13}\Sigma x_1y + C_{23}\Sigma x_2y + C_{33}\Sigma y\right)
\end{aligned}$$

The standard deviations in the correlation coefficients are obtained in terms of the standard deviation of the entire correlation, $\delta^2$, as obtained from

$$\delta^2 = \frac{\Sigma y^2 - b_1\Sigma x_1y - b_2\Sigma x_2y - b_0\Sigma y}{n - 3}$$

Then the standard deviation in $b_1$ is $(C_{11}/D)\ \delta^2$, in $b_2$ is $(C_{22}/D)\ \delta^2$, and in $b_0$ is $(C_{33}/D)\ \delta^2$. The multiple correlation coefficient, $R$, is obtained from the expression

$$R = \left[\frac{b_1\Sigma x_1y + b_2\Sigma x_2y + b_0\Sigma y - 1/n(\Sigma y)^2}{\Sigma y^2 - 1/n(\Sigma y)^2}\right]^{1/2}$$

In using the above relationships to obtain the best fit of the methanolysis rates to equation 1, several definitions are made

$y = \log k$, $x_1 = \sigma^*$, $x_2 = E_s$, $b_0 = \log k_0$, $b_1 = \rho^*$, and $b_2 = \delta$

**Acknowledgment.**—The authors are indebted to Mr. Robert Nieman for determining the rate of alkaline saponification of ethyl cyanoacetate and to Mr. Richard A. Javick for determining the rate of the acid-catalyzed hydrolysis of this ester.

UNIVERSITY PARK, PENNA.

---

[20] R. W. Taft, Jr., THIS JOURNAL, **75**, 4534 (1953); *cf.* reference **11c**, p. 665.

[21] R. L. Anderson and T. A. Bancroft, "Statistical Theory in Research," McGraw-Hill Book Co., Inc., New York, N. Y., 1952, Chapt. **14**.

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

# γ-Ray Initiated Reactions.[1] I. The Addition of Bromotrichloromethane to Alkenes

BY EL-AHMADI I. HEIBA[2] AND LEIGH C. ANDERSON

RECEIVED AUGUST 20, 1956

The reaction of bromotrichloromethane with a number of alkenes under the effect of γ-rays is described. 1-Substituted alkenes gave 1:1 addition products of the general formula $R\text{–}CHBr\text{–}CH_2\text{–}CCl_3$, but cyclic alkenes revealed beside the 1:1 addition products the corresponding 1,2-dibromo- and the 1,2-ditrichloromethyl compounds. The 1,1-disubstituted alkene, α-methylstyrene, gave a dimer of the general formula $[Cl_3CCH_2CRR'\text{–}]_2$ in addition to the 1:1 addition product. 1,2-Disubstituted alkenes gave poor yields of the 1:1 addition product; with 1,2-dibromoethene, equimolecular quantities of $Cl_3C\text{—}CH{=}CHBr$ and $CHBr_2CHBr_2$ were the only products isolated.

The addition of bromotrichloromethane to unsaturated compounds under the influence of ultraviolet light or initiated with peroxides has been studied by previous investigators. This work presents data obtained from studies of similar reactions at room temperature, using γ-radiation from a 3.5 kilo-curie $Co^{60}$ source as the activating agent. With a number of alkenes the products obtained with γ-radiation were the same as those formed with ultraviolet radiation or peroxides, but under the conditions used in this work there were a number of different reactions observed.

Octene-1, indene, butene-2, allyl chloride, allyl cyanide, ethyl cinnamate and *cis*- and *trans*-1,2-dichloroethene gave 1:1 addition products, as obtained with ultraviolet and peroxide initiators.

Kharasch and Friedlander[3] noted that there was little reaction between bromotrichloromethane and

---

[1] These studies were supported by Michigan Memorial Phoenix Project No. 98 given by the Chrysler Corporation. Some assistance was obtained from Atomic Energy Commission contract No. AT(11-1)-162 under the joint supervision of Leigh C. Anderson and Joseph J. Martin of the Department of Chemical Engineering.

[2] Study in leave from the Department of Chemistry, Faculty of Science, A'in Shams University, Cairo, Egypt.

[3] M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949).