Correlations between Structure and Nuclear Magnetic Resonance Spectra for Aliphatic Esters[1]

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Received February 3, 1966

The nmr chemical shifts have been measured for 18 acetate esters, CH_3COOR', and 16 methyl esters, $RCOOCH_3$, neat, and in carbon tetrachloride solution. The nmr chemical shifts of the acetates are controlled largely by polar and C-6 atom effects of the R′ group while the nmr chemical shifts of the methyl esters are controlled partially by polar and hyperconjugation effects of the R group. The C-6 effect of the R′ group has been explained in terms of inhibition of resonance. The presence of rotational isomers could not be detected at high and low temperatures.

The alkaline hydrolysis rate constants for saturated esters, $RCOOR'$, are affected by polar, steric, and hyperconjugation effects of the R group and by polar and steric effects of the R′ group.[3] Further, Newman[4] has shown that for the esterification of carboxylic acids and the hydrolysis of esters, the 6 no. of a substituent (*i.e.*, the number of atoms in the 6 position from the carbonyl oxygen atom as atom no. 1) makes a large contribution to the total steric effect of that substituent.

The alkaline hydrolysis rate constants[3] for a series of nine methyl esters, $RCOOCH_3$, in 40% aqueous *p*-dioxane at 35° agree quite closely with eq 1 obtained by multiple regression analysis.[5a] In eq 1, k is the

$$\log k = 1.25 + \underset{(100.0)}{1.75\sigma^*} + \underset{(100.0)}{0.848E_s^c} - \underset{(100.0)}{0.383(n-3)}; \quad R = 0.998,\ s = 0.043 \qquad (1)$$

second-order rate constant, σ^* is Taft's polar substituent constant,[6a] E_s^c is Taft's steric substituent constant[6b] corrected[3] for hyperconjugation effects, n is the number of α hydrogens in the R group, R is the multiple correlation coefficient,[5a] and s is the standard deviation from regression.[5a] The numbers in parentheses below the three coefficients of eq 1 are the percentage confidence levels as determined by "Student's" t tests.[5b]

Equation 2 has been obtained[7] for the alkaline hydrolysis rate constants of nine acetate esters in aqueous

$$\log k = 1.35 + \underset{(95.5)}{0.688\sigma^*} + \underset{(100.0)}{0.644E_s^c} + \underset{(99.6)}{0.0477(\Delta 6)}; \quad R = 0.997,\ s = 0.070 \qquad (2)$$

p-dioxane at 35°. In this equation, Δ6 is the change in the 6 no.;[4] *i.e.*, the difference of the 6 no. of a substituent in the R part of the ester minus the 6 no. of the same substituent in the R′ part of the ester.

In view of the excellent correlations of eq 1 and 2, it appeared to be of interest to study the chemical shifts of the methyl hydrogens in CH_3COOR' and in $RCOOCH_3$ relative to the corresponding methyl hydrogens in methyl acetate. This study was carried out independently of but more or less simultaneously with that of Kan[8] who measured the chemical shifts, relative to methyl acetate, of 26 acetates, CH_3COOR', in carbon tetrachloride solution and concluded qualitatively that the chemical shifts are controlled largely by polar and 6-no. effects[4] of the R′ group.

Results and Discussion

Acetate Esters, CH_3COOR'.—For each of 18 acetate esters, the difference between the chemical shift of the acetyl methyl protons of CH_3COOR' minus the chemical shift of the corresponding protons of CH_3COOCH_3 is shown in Table I.

In view of eq 2 for the alkaline hydrolysis rate constants for acetate esters, it was desired to evaluate polar (σ^*), steric (E_s^c), change in the 6 no. (Δ6), and, as suggested by Kan,[8] 6 no. effects of the R′ group on the chemical shift of the acetyl methyl protons of acetate esters, CH_3COOR'. Consequently, using Kan's data[8] for 21 acetates ($R' = CF_3CH_2$, $CH_2=CHCH_2$, C_6H_5, CH_3CO, and CH_3COCH_2 omitted either because of conjugation or because no E_s^c value is available), eq 3 is obtained.

$$\text{cps} = 0.383 + \underset{(100.0)}{8.37\sigma^*} - \underset{(91.0)}{0.715E_s^c} + \underset{(92.4)}{0.190(\Delta 6)} - \underset{(69.0)}{0.252(6\text{ no.})}; \quad R = 0.949,\ s = 0.761 \qquad (3)$$

Rejecting the least significant variable, 6 no., eq 4 is obtained.

$$\text{cps} = -0.077 + \underset{(100.0)}{9.09\sigma^*} - \underset{(89.1)}{0.365E_s^c} + \underset{(100.0)}{0.279(\Delta 6)}; \quad R = 0.946,\ s = 0.763 \qquad (4)$$

Rejecting the next least significant variable, E_s^c, eq 5 is obtained.

$$\text{cps} = 0.336 + \underset{(100.0)}{8.14\sigma^*} + \underset{(100.0)}{0.291(\Delta 6)}; \quad R = 0.936,\ s = 0.801 \qquad (5)$$

Thus, it appears that the relative chemical shift is controlled largely by σ^* and Δ6 and that 6 no. and E_s^c are statistically insignificant variables.

Even though eq 5 indicates that Δ6 is a highly significant variable, it is difficult to provide a theoretical basis for its pertinence in this case. As proposed,[7] Δ6 is nothing more than a necessary correction of E_s^c when used for the R′ group of $RCOOR'$. As can be seen in eq 3 and 4, E_s^c is not a statistically significant variable. Consequently, it appears that the use of a correcting variable, Δ6, for an impertinent variable, E_s^c, is without meaning. Probably, Δ6 appears to be pertinent

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[1] Abstracted in part from the Ph.D. Dissertation of O. R.-L., Texas A and M University, Aug 1965.

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[7] C. K. Hancock, B. J. Yager, C. P. Falls, and J. O. Schreck, *J. Am. Chem. Soc.*, **85**, 1297 (1963).

[8] R. O. Kan, *ibid.*, **86**, 5180 (1964).

TABLE I

CHEMICAL SHIFT CHANGES AND SUBSTITUENT CONSTANTS FOR 18 ACETATE ESTERS, CH_3COOR'

	Shift of CH_3COOR' from CH_3COOCH_3, cps, 37°				Substituent constants			
R′ in CH_3COOR'	Neat[a] *vs.* TMS[b]	In CCl_4 *vs.* CH_3COOCH_3	In CCl_4[c] *vs.* TMS	σ^* [d]	E_s° [e]	6 no.[f]	Δ6[g]	C-6 no.[h]
CH_3	0.0	0.0	0.0	0.000	0.00	0	0	0
C_2H_5	−1.3	−0.9	−1.0	−0.100	−0.38	3	−3	0
n-C_3H_7	−1.1	−0.3	−0.4	−0.115	−0.67	3	0	1
n-C_4H_9	−1.9	−0.8	−0.9	−0.130	−0.70	3	0	1
n-C_5H_{11}	−2.1	−0.9	−0.9	−0.162[i]	−0.71	3	0	1
i-C_3H_7[j]	−2.7	−2.5	−2.5	−0.190	−1.08	6	−6	0
t-C_4H_9[j,k]	−6.5	−5.5	−5.6	−0.300	−2.46	9	−9	0
i-C_4H_9	−0.9	0.0	0.0	−0.125	−1.24	3	3	2
t-$C_4H_9CH_2$	0.0	+1.1	+1.0	−0.165	−2.05	3	6	3
$(C_2H_5)_2CH$	−1.1	0.0	0.0	−0.225	−2.59	6	0	2
s-C_4H_9[j]	−1.9	−1.7	−1.6	−0.210	−1.74	6	−3	1
t-$C_4H_9C(CH_3)_2$[j,k]	−6.3	−4.2	−4.5	−0.365[l]	−4.82	9	0	3
(*i*-$C_4H_9)_2CH$	−3.5	−1.4	−1.8	−0.260	−3.08	6	0	2
i-$C_3H_7CH(CH_3)$	−2.3	−1.2	−1.0	−0.225[l]	. . .	6	0	2
$C_2H_5C(CH_3)_2$	−6.0	−4.7	−4.8	−0.315[l]	. . .	9	−6	1
$(C_2H_5)_2C(CH_3)$	−5.9	−4.2	−4.3	−0.330[l]	. . .	9	−3	2
i-$C_4H_9CH(CH_3)$	−3.5	−2.2	−2.3	−0.230[l]	. . .	6	−3	1
i-C_5H_{11}	−1.3	−0.8	−0.7	−0.130	−0.66	3	0	1

[a] Shift of CH_3COOCH_3 (neat) *vs.* TMS is 118.5 cps. [b] Tetramethylsilane. [c] Shift of CH_3COOCH_3 *vs.* TMS (in CCl_4) is 119.2 cps. [d] Ref 6a. [e] Ref 6b and 3. [f] Ref 4. [g] Ref 7. [h] Number of carbon atoms in the 6 position. [i] A. B. Hoefelmeyer and C. K. Hancock, *J. Am. Chem. Soc.*, **77**, 4746 (1955). [j] Chemical shift also measured (neat) at −40 and +120°. [k] Chemical shifts also measured at 37° in methanol and in chloroform. [l] σ^* calculated by Taft's additivity principle.[6c]

because it is related to the number of six carbons (C-6 no.) which is a pertinent variable as shown below. Consequently, using Kan's data[8] for the same 21 esters as used in eq 3–5, correlation gives eq 6.

$$\text{cps} = -0.783 + \underset{(100.0)}{9.91\sigma^*} + \underset{(99.8)}{0.845(\text{C-6 no.})};\ R = 0.907,\ s = 0.961 \tag{6}$$

Using comparable data from the third and second columns of Table I for 18 acetates, correlation gives eq 7 for the esters in carbon tetrachloride solution and eq 8 for the esters neat. Both eq 7 and 8 account for 89% of the variance of cycles per second.

$$\text{cps} = 0.953 + \underset{(100.0)}{20.4\sigma^*} + \underset{(100.0)}{1.11(\text{C-6 no.})};\ R = 0.943,\ s = 0.659 \tag{7}$$

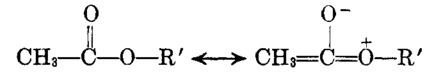
$$\text{cps} = 0.990 + \underset{(100.0)}{23.8\sigma^*} + \underset{(99.8)}{0.825(\text{C-6 no.})};\ R = 0.941,\ s = 0.772 \tag{8}$$

The differences between corresponding parameters in eq 6 and 7 are largely due to differences between the two series of esters involved (eq 6 involves 21 esters, eq 7 involves 18 esters, and only 11 esters are common to the two series).

If the ρ^* values of 9.91, 20.4, and 23.8 of eq 6–8 are compared with that of 0.688 of eq 2, it might be inferred that the transmission of polar effects for chemical shifts is much greater than that for alkaline hydrolysis. Such an inference is misleading because the energy quantities involved in chemical shifts are so much less than those involved in alkaline hydrolysis and also the ρ^* value of eq 2 is dimensionless while those of eq 6–8 have dimensions of cycles per second. The ρ^* values of eq 6–8 could have been made dimensionless by expressing chemical shifts as parts per million but this would have resulted in no material advantage.

Since the C-6 no. is somewhat related to the 6 no. itself, the significance of σ^* and C-6 no. are in partial accord with Kan's[8] qualitative conclusion that the chemical shifts are largely controlled by polar and 6-no. effects.

In order to explain his results, Kan[8] considered the existence of resonance forms I and II for acetates. If the contribution of form II to the hybrid is important,



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-R' \longleftrightarrow CH_3=\overset{\overset{\displaystyle O^-}{|}}{C}=\overset{+}{O}-R'$$

I II

electron donation by R′ should be transmitted more easily and increase the electron density at the acetyl methyl protons, thereby shifting the nmr absorption of the acetyl methyl protons toward higher field. Conversely, if the contribution of form II to the hybrid is less important, the nmr absorption of the acetyl methyl protons tends to be shifted toward lower field.

Kan concluded[8] that steric inhibition of form II is more probable when the carbon connected to the oxygen atom possesses groups larger than methyl.

The positive sign for the coefficient ρ^* of σ^* in eq 6–8 is theoretically correct since it indicates that the electron density around the acetyl methyl protons is increased by increase in the electron-donating power of R′. At the same time the positive coefficient of C-6 no. indicates that the electron density around the acetyl methyl protons decreases as the number of carbons in the 6 position increases.

Thus, there is strong indication that steric inhibition of resonance between I and II is more pronounced for carbon atoms in the 6 position than for hydrogen atoms in the 6 position and this explains why the 6 no., which is the sum of the number of carbon atoms and hydrogen atoms in the 6 position, is not a significant variable in the correlation of chemical shifts.

Perhaps, the correlations of eq 6–8 are no better because the polar and 6-carbon effects are operating over a greater distance in chemical shifts of the acetyl methyl protons than in the case of alkaline hydrolysis at the carbonyl carbon. It is difficult to deal with these differences in distance since, in each case, the mean

TABLE II

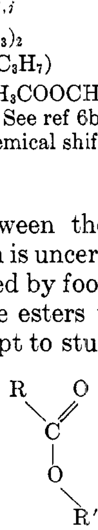
CHEMICAL SHIFT CHANGES AND SUBSTITUENT CONSTANTS FOR 16 METHYL ESTERS, $RCOOCH_3$

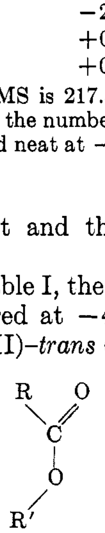
R in $RCOOCH_3$	Shift of $RCOOCH_3$ from CH_3COOCH_3, cps, 37°: Neat[a] *vs.* TMS[b]	In CCl_4 *vs.* CH_3COOCH_3	In CCl_4[c] *vs.* TMS	Substituent constants: σ^* [d]	E_s^c [e]	$(n - 3)$[f]	6 no.[g]
CH_3	0.0	0.0	0.0	0.000	0.00	0	0
C_2H_5	+0.1	+0.7	+0.7	−0.100	−0.38	−1	0
n-C_3H_7	−0.5	+0.4	+0.4	−0.115	−0.67	−1	3
n-C_4H_9	−1.0	0.0	+0.2	−0.130	−0.70	−1	3
n-C_5H_{11}	−1.2	0.0	+0.1	−0.162	−0.71	−1	3
i-C_3H_7	−0.1	+0.8	+0.7	−0.190	−1.08	−2	0
t-C_4H_9[h]	+0.2	+0.8	+0.5	−0.300	−2.46	−3	0
i-C_4H_9	−0.4	0.0	0.0	−0.125	−1.24	−1	6
t-$C_4H_9CH_2$[i]	−1.4	0.0	−0.3	−0.165	−2.05	−1	9
$(C_2H_5)_2CH$[i,j]	+0.6	+1.2	+0.8	−0.225	−2.59	−2	6
s-C_4H_9	+0.2	+0.8	+0.9	−0.210	−1.74	−2	3
$C_2H_5C(CH_3)_2$	−0.6	+0.7	+0.3	−0.315	...	−3	3
$(C_2H_5)_3C$[j]	−0.4	+0.7	+0.7	−0.345	−4.72	−3	9
$(t$-$C_4H_9)_2CH$[i,j]	−3.5	−2.2	−2.5	−0.330	...	−2	18
n-$C_3H_7C(CH_3)_2$	−1.3	+0.4	+0.1	−0.330	...	−3	3
i-$C_4H_9CH(i$-$C_3H_7)$	−1.1	+0.4	0.0	−0.225	...	−2	9

[a] Shift of CH_3COOCH_3 (neat) *vs.* TMS is 217.5 cps. [b] Tetramethylsilane. [c] Shift of CH_3COOCH_3 *vs.* TMS (in CCl_4) is 217.2. [d] See ref 6a. [e] See ref 6b and 3. [f] n is the number of α hydrogens in the R group. [g] See ref 4. [h] Chemical shift also measured neat at 100°. [i] Chemical shift also measured neat at −50 and +125°. [j] Chemical shift also measured at 37° in methanol and in chloroform.

distance between the substituent and the center in consideration is uncertain.

As indicated by footnote *j* to Table I, the nmr spectra of four of the esters were measured at −40 and 120° in an attempt to study the *cis* (III)-*trans* (IV) equilibrium, but no changes were observed in the spectra in agreement with Kowalewski's studies of some alkyl formates[9] and acetates[10] and the assigned rigid structure of alkyl esters.[11]


III (*cis*)


IV (*trans*)

The possibility of intramolecular hydrogen bonding between the hydrogens in the 6 position and the carbonyl oxygen atom was considered. However, studies in solvents which form hydrogen bonds of different strengths (carbon tetrachloride, methanol, and chloroform) showed no significant change in the chemical shift for those particular hydrogens.

Methyl Esters, $RCOOCH_3$.—For each of 16 methyl esters, the difference between the chemical shift of the alkyl methyl protons of $RCOOCH_3$ minus the chemical shift of the corresponding protons of CH_3COOCH_3 is shown in Table II.

Since eq 1 shows that the alkaline hydrolysis rate constants for methyl esters are controlled by polar, steric, and hyperconjugation effects, it was desired to evaluate these effects of the R group on the chemical shift of the alkyl methyl protons of $RCOOCH_3$.

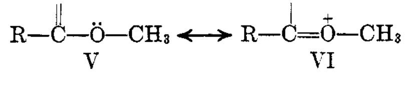
The changes observed in the chemical shifts for methyl esters in carbon tetrachloride are smaller than the ones observed in corresponding acetate esters. As substitution on the α carbon increases, the expected shift to a higher field of the nmr absorption of alkyl methyl protons is not observed but rather a small shift to lower field is observed. This means that the electron density around the alkyl methyl protons does not increase with the decreasing value of σ^* but decreases as if the substituents were becoming more weakly electron-withdrawing, which is not the case.

This behavior can be explained if hyperconjugation effects are considered since, as α branching in the R group increases, the number of α hydrogens decreases and hyperconjugation effects decrease. Similar behavior has been encountered in studies of N-substituted pyrazoles[12] and alkyl- and alkoxybenzenes.[13]

An increase in chain length and β branching of the R group seem to have no effect on the chemical shift of the alkyl methyl protons. However, a large chemical shift to a higher field is observed when two *t*-butyl groups are connected to the α carbon.

As the $(t$-$C_4H_9)_2CH$ group has the same σ^* value as the n-$C_3H_7C(CH_3)_2$ group, contributions of the polar effect for these two groups should be the same. The difference between hyperconjugation effects for these two groups is not sufficient to account for the large difference of 2.6 cps between the corresponding chemical shifts since the i-C_3H_7 and t-C_4H_9 groups, with the same difference between hyperconjugation effects, show no difference in chemical shift. Thus, hyperconjugation effects alone cannot account fully for the chemical shifts given in the third column of Table II.

In structure VI, where the ethereal oxygen atom bears a positive charge, the electron density around the alkyl methyl protons should be smaller than in structure V in which there are two more unshared electrons on the oxygen atom.


$$\underset{\text{V}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-\ddot{O}-CH_3} \longleftrightarrow \underset{\text{VI}}{R-\overset{\overset{\displaystyle O^-}{|}}{C}=\overset{+}{\ddot{O}}-CH_3}$$

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(9) D. G. de Kowalewski and V. J. Kowalewski, *Mol. Phys.*, **8**, 93 (1964).

(10) V. J. Kowalewski, Facultad de Ciencias Exactas y Naturales, University of Buenos Aires, Buenos Aires, Argentina, private communications.

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The presence of two *t*-butyl groups in the α position of R greatly increases the number of atoms in the 6 position.[4] These 6 atoms approach the carbonyl oxygen atom forcing it from the coplanarity necessary for form VI, producing steric inhibition of resonance, and probably increasing the electron density around the alkyl methyl protons.

For the 12 methyl esters of Table II for which E_s^c values are available, the correlation of the chemical shift of the alkyl methyl protons with σ^*, E_s^c, and $(n - 3)$ gives an equation with E_s^c being the least significant variable (30.5% confidence level). Rejecting E_s^c, correlation gives an equation in which $(n - 3)$ is significant (98.5% confidence level) and σ^* is nearly significant (93.0% confidence level). Since σ^* and $(n - 3)$ values are available for all 16 of the methyl esters, the latter correlation was repeated on the data for all of these 16 esters to give eq 9 which represents a fair over-all correlation (accounts for 74.5% of the variance of cycles per second) and indicates that both σ^* and $(n - 3)$ are highly significant variables.

$$\text{cps} = 0.446 + \underset{(100.0)}{18.4\sigma^*} - \underset{(100.0)}{2.06(n - 3)};\ R = 0.863,\ s = 0.415 \qquad (9)$$

The negative sign for the coefficient of $(n - 3)$ in eq 9 is theoretically correct since it indicates that the electron density around the alkyl methyl protons is decreased by a decrease in the number of α hydrogens in the R group.

With only alkyl groups present as R of $RCOOCH_3$, as the number of α hydrogens decreases, the value of σ^* simultaneously decreases (becomes more negative). The positive coefficient of σ^* in eq 9 shows that the electron density around the alkyl methyl protons tends to be increased by a decrease in σ^*. Thus, the chemical shifts of methyl esters are controlled mainly by two simultaneous opposing effects which tend to cancel each other and this accounts for the relatively small chemical shifts for the methyl esters.

Similar results were obtained for the methyl esters neat.

In an attempt to explain the order of ionization constants of acids, hydrogen bonding between the hydrogen atoms in the 6 position and the carbonyl oxygen atom has been proposed.[14,15] Studies in different solvents of increasing hydrogen bonding power showed no changes in the nmr spectra for these 6 hydrogens, ruling out the possibility of hydrogen bonding.

Studies at temperatures ranging from −50 to 125° for three of the esters marked in Table II showed no changes in the nmr spectra with temperature.

Experimental Section

Methyl di-*t*-butylacetate was prepared by treating the corresponding acid[16] with diazomethane[17] (prepared from Diazald, N-methyl-N-nitroso-*p*-toluenesulfonamide): bp 193–194° (753 mm), $n^{25}D$ 1.4331.

Anal. Calcd for $C_{11}H_{22}O_2$: C, 70.92; H, 11.90. Found:[18] C, 70.36; H, 11.90.

Methyl isopropylisobutylacetate was prepared by treating 3-bromo-2,6-dimethyl-4-heptanone with an ethereal suspension of sodium methoxide[19] (free of methanol): bp 176° (752 mm), $n^{25}D$ 1.4163.

Anal. Calcd for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70. Found:[18] C, 69.76; H, 11.60.

The majority of the other 31 esters used in this study were purchased. The remainder of the esters were prepared by reaction between the appropriate acyl chloride and alcohol in pyridine or in N,N-dimethylaniline solution, the choice of solvent being determined by the boiling point of the ester. All 33 esters were purified by fractional distillation as described previously.[8]

Nmr Spectral Measurements.—Using a Varian A-60 spectrometer with variable-temperature probe, the chemical shifts with respect to tetramethylsilane as internal standard of the esters neat and in carbon tetrachloride solution were measured at 37° at 250-cycle chart width and are accurate to about 0.2 cps. Chemical shifts, with respect to methyl acetate as internal standard,[8] of the esters in carbon tetrachloride solution were also measured at 37°, but at 50-cycle chart width, and are accurate to about 0.1 cps. The concentration of all samples in carbon tetrachloride solution was 100 mg of ester/ml of solvent (the solution also contained 50 mg of methyl acetate/ml of solvent when this ester was used as an internal standard). The chemical shifts relative to methyl acetate are shown in Tables I and II. The spectra have been contributed to the "Catalog of NMR Spectra" of the MCA Research Project and may be found there.[20]

Acknowledgments.—This study was supported in part by a research grant from The Robert A. Welch Foundation. The statistical calculations were performed by the Data Processing Center, Texas Engineering Experiment Station, College Station, Texas, on an IBM-7094 computer. Technical assistance of L. L. Altpeter on the nmr spectra is gratefully acknowledged.

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[19] J. G. Aston and J. D. Newkirk, *J. Am. Chem. Soc.*, **73**, 3900 (1951).

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