Basicity of Aliphatic Esters[1]

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Abstract: Chemical shift data have been used to evaluate an acidity function (H_E) applicable to aliphatic esters, for aqueous solutions containing from 60 to 98% H_2SO_4. The function appears to adequately define the protonation behavior of several simple, unsubstituted aliphatic esters; however, esters which bear substituents near the site of protonation exhibit unique responses to acidity changes. The suggestion is made that these latter esters do not conform well to the H_E function primarily because substitution causes substantial changes in the solvation requirements of the conjugate acid of each compound.

A quantitative measurement of the basicity of organic compounds is an important problem for investigation because of the large number of reactions which are subject to acid catalysis. A knowledge of the pK_{BH^+} values of the compounds involved is essential for a complete understanding of such reactions. Beginning with the work of Hammett and Deyrup[2] about 40 years ago considerable evidence concerning the basicity and protonation behavior of many aromatic compounds has been accumulated. However, quantitative knowledge with respect to aliphatic compounds is much less abundant, primarily because it is more difficult to determine the extent of protonation of these compounds conveniently and accurately. Despite these difficulties work on the basicity of aliphatic compounds is worthwhile pursuing because of the potential importance of the results to an understanding of the numerous organic and biochemical reactions in which they are involved.

Among the most frequently encountered and important organic compounds are the aliphatic esters, and consequently we have attempted to determine the basicities of several of them by using nmr chemical shifts as an index of protonation. It has been shown from the results of several investigations[3,4] that nuclear magnetic resonance spectroscopy can be used to estimate the extent of protonation of aliphatic compounds, although with less precision than is usually possible when the presence of aromatic chromophores permit the use of ultraviolet–visible absorption spectroscopy. For the present study we have used a procedure in which the difference between the chemical shifts of the α and β hydrogens (Δ) is taken as a measure of the extent of protonation. This method rests on the assumption that the chemical shifts of the α hydrogens will be more greatly affected by protonation than those of the β hydrogens. Since the nmr time scale is relatively long and the protonation–deprotonation of esters very rapid,

a time and species averaged chemical shift is observed for a given proton resonance. Thus, at a particular acidity corresponding to partial protonation, the observed chemical shift of a proton is a weighted average of the unprotonated and protonated esters. The procedure has an advantage over the use of absorption spectroscopy for compounds, such as esters, which tend to undergo reactions in aqueous acid solutions. Any significant amount of reaction will interfere with a method using ultraviolet spectral changes as an indication of protonation; however, because the nmr method utilizes the *position* of the signals and not their *intensity*, chemical reactions (provided they are not rapid equilibria) do not interfere with the nmr method as long as the signals from the products do not mask those of the unreacted compound. Using chemical shift differences (Δ) has the added advantage that since all the atoms in a simple small molecule would be in approximately the same environment any solvent effects should be minimized.

However, being able to measure the extent of protonation of a compound in a particular solution does not permit one to calculate basicity constants (pK_{BH^+} values) directly; the results must first be expressed in terms of an acidity scale or function. In attempting to do this three approaches are available: (i) the data can be analyzed in terms of a well-established scale such as the Hammett acidity function[5] (H_0); (ii) the Bunnett–Olsen[6] approach can be used; or (iii) an attempt can be made to establish a new independent function for the particular type of compound under consideration. As will be described we have applied all three of these approaches to our data. However, before examining the actual results it is instructive to consider the advantages and, particularly, the limitations of each approach.

The Hammett acidity function (H_0) as expressed in eq 1 (where I is the ratio of protonated and free base

$$\log I = -H_0 + pK_{BH^+} \tag{1}$$

present, $[BH^+]/[B]$) pertains exactly to only one type of base—the primary aromatic amines. However, since most acidity functions are known to be approximately linear with respect to each other it is possible to generalize eq 1 by insertion of a factor, m, which corresponds to the slope of the required acidity function with

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(6) J. F. Bunnett and F. P. Olsen, *Can. J. Chem.*, **44**, 1899, 1917 (1966).

respect to H_0. The resulting eq 2 then indicates that

$$\log I = -mH_0 + pK_{BH^+} \qquad (2)$$

the pK_{BH^+} of a compound is approximately equal to the product of the slope, m, times the intercept on the axis of abscissas of a plot of $\log I$ vs. $-H_0$. The intercept of such a plot would correspond to the acidity, as expressed in H_0 units, where the base is one-half protonated. While it is undoubtedly true that most acidity functions are linear with respect to each other over short ranges, eq 2 must be used with caution because it assumes a linearity from the point of one-half protonation of a compound down to the pH region—an extrapolation that often involves 4–8 logarithmic units! Any nonlinearity between the two scales is a potential source of error in the basicity constant obtained. Nevertheless this approach has been used with apparent success by other workers who have previously been interested in the protonation of aliphatic esters.[7-9]

Bunnett and Olsen[6] have suggested that the possibility of nonlinearity between various acidity scales can be minimized by use of eq 3, which has been derived and

$$\log I + H_0 = \phi(H_0 + \log[H^+]) + pK_{BH^+} \qquad (3)$$

discussed elsewhere.[6,10] Although no one has previously attempted to use this approach with esters, the results obtained with a wide variety of other compounds are impressive.[6,11] On the other hand, the relationship apparently fails in very concentrated acid solutions (above about 85%) and as a consequence the pK_{BH^+} values of very weak bases cannot be obtained in this way.

The third possible approach to the problem of ester basicity is to develop a new acidity function, as defined by eq 4, which is based directly on the use of aliphatic

$$H_E = -\log I + pK_{BH^+} \qquad (4)$$

esters as indicators. Ideally this could be done using the well-known overlap technique[2,3,10] to build up the scale from the pH region. Unfortunately, such an approach will never be completely possible because no aliphatic esters are appreciably protonated in dilute acid solutions where pH measurements can be made. Instead, it is necessary to first define, as satisfactorily as possible, the pK_{BH^+} of one ester which can then be used as the initial indicator. In our work, as will be described, we have attempted to develop an H_E function by first defining the pK_{BH^+} of ethyl acetate through application of the Bunnett-Olsen equation. However, it must be remembered that any error in the calculated basicity of the initial indicator is transmitted to, and often enhanced in, all the other compounds when this method is used.

Experimental Section

All the esters were obtained commercially and purified by vacuum distillation until a single peak was obtained for each compound

by glc analysis. Sulfuric acid solutions up to 95% were prepared by diluting reagent grade acid with doubly distilled water. Acid solutions of higher concentrations were obtained by addition of fuming sulfuric acid (20% SO_3). Standardization was accomplished by titrating weighed amounts of each sulfuric acid solution with standardized sodium hydroxide solutions. The H_0 values up to 98% H_2SO_4 are those reported by Jorgenson and Hartter[5] and beyond 98% H_2SO_4 those of Gillespie, et al.[12]

All spectra were obtained using a Varian A-60A spectrophotometer. Each measurement was made by adding 0.10 ml of the base to 5.0 ml of standardized acid in a volumetric flask. After inverting the flask several times to ensure homogeneity, a small portion was transferred to an nmr tube and the spectrum recorded at 37 ± 1°. Since only the difference in the chemical shift is required no internal standard was used. The instrument was carefully tuned using TMS and chloroform as standards and a frequent sweep width calibration was done using a signal generator. Typical data for one ester, ethyl acetate, are given in Table I.

Table I. Chemical Shift Data for Ethyl Acetate

% H_2SO_4	Δ, Hz	Log I	% H_2SO_4	Δ, Hz	Log I
19.2	174.5		67.0	178.5	−0.80
32.8	175.0		67.7	179.5	−0.67
35.8	174.5		70.6	180.0	−0.61
44.6	175.0		73.7	181.5	−0.46
47.6	175.5		74.7	182.5	−0.38
49.1	175.5		75.3	183.0	−0.34
51.7	174.5		77.4	185.8	−0.13
53.3	174.5		80.9	189.0	0.12
56.0	175.5		82.8	191.0	0.22
57.3	175.8		85.4	196.3	0.70
57.9	176.0		86.1	197.0	0.80
60.0	177.0	−1.07	88.4	198.0	0.96
62.3	177.0	−1.07	93.7	200.5	
66.4	177.5	−0.96	97.6	200.5	

There are two important potential sources of error in this work: (i) the addition of organic compounds introduces a constant error into the reported sulfuric acid concentrations, and (ii) errors are encountered in the measurement of chemical shifts. No corrections were made for the first of these sources of error; however, an attempt was made to take the latter, which is probably more important, into consideration. It was observed that the chemical shift differences were reproducible to within about 0.5 Hz with somewhat better resolution being obtained in the region of 60–90% H_2SO_4. Since I is a ratio, $[BH^+]/[B] = (\Delta - \Delta_B)/(\Delta_{BH^+} - \Delta)$ where Δ_B is the chemical shift difference between two selected sets of hydrogens of the unprotonated ester, Δ_{BH^+} is the difference between the chemical shifts of the same hydrogens in the completely protonated ester, and Δ the corresponding value when the ester is partially protonated, it is necessary to assume a possible error of ±0.5 Hz in both the numerator and the denominator. Consequently a computer program which allowed us to do this routinely was written and the error limits reported in this paper are all based on the possibility of errors of this magnitude in the values of I. In this respect they represent not the maximum possible errors, but an educated estimate of the reliability of our results.

The use of esters such as ethyl propionate and ethyl 3-chloropropionate allows for the possibility of obtaining Δ values by using a number of different sets of hydrogens. For example, in ethyl 3-chloropropionate the following combinations may be used: α(alkyl)–β(alkyl), α(acyl)–α(alkyl), β(acyl)–α(alkyl), α(acyl)–β(alkyl), β(acyl)–α(acyl), and β(acyl)–β(alkyl). The variation in I values using these combinations is indicated in Table II and the parameters obtained by using each set of I values in eq 2 and 4 are compared in Table III. From an examination of the contents of these tables it is clear that the results are identical for each set of data within the experimental uncertainties established by allowing for a possible error of 0.5 Hz in Δ. It would seem reasonable to assume, however, that the results obtained when the difference between Δ_B and Δ_{BH^+} is largest would be the most accurate, and we have, consequently, chosen to use the difference between the chem-

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Table II. Chemical Shift Differences Obtained Using All Possible Combinations of Hydrogens in Ethyl 3-Chloropropionate

% H₂SO₄	Δ,ᵃ Hz	Log I	Δ,ᵇ Hz	Log I	Δ,ᶜ Hz	Log I	Δ,ᵈ Hz	Log I	Δ,ᵉ Hz	Log I	Δ,ᶠ Hz	Log I
62.3	177.0		81.0		151.5		96.5		55.0		25.5	
64.0	177.5		80.5		151.5		97.0		55.0		25.5	
67.7	178.0	−1.36	81.0		151.0	−1.41	97.0		54.0	−1.40	27.0	−1.38
70.6	178.0	−1.36	81.0		150.5	−1.10	97.0		53.4	−1.21	27.5	−1.25
73.7	180.0	−0.85	82.0	−0.95	150.5	−1.10	98.0	−1.04	52.5	−0.97	29.5	−0.92
75.7	180.5	−0.77	82.5	−0.75	150.0	−0.90	98.0	−1.04	52.0	−0.88	30.5	−0.81
77.4	181.0	−0.70	83.0	−0.60	149.5	−0.76	98.0	−1.04	51.5	−0.81	31.5	−0.72
82.8	185.0	−0.30	84.0	−0.37	147.0	−0.38	100.5	−0.39	47.0	−0.35	37.5	−0.33
85.1	189.0	0.00	85.5	−0.09	145.5	−0.10	103.5	0.07	42.0	0.00	43.5	−0.31
86.6	191.5	0.18	86.5	0.09	144.5	0.03	105.0	0.30	39.5	−0.17	47.0	0.13
87.7	191.0	0.15	87.0	0.18	144.5	0.03	104.0	0.15	40.5	0.10	46.5	0.10
89.5	196.5	0.64	89.0	0.60	140.5	0.64	107.5	0.85	33.0	0.74	56.0	0.64
92.6	197.0	0.70	89.5	0.75	142.0	0.38	107.5	0.85	34.5	0.57	55.0	0.57
93.7	198.5	0.93	90.0	0.95	140.5	0.64	108.5	1.36	32.0	0.88	58.0	0.81
95.1	200.0	1.36	91.0		139.5	0.90	109.0		30.5	1.21	60.5	1.15
96.1	199.0	1.04	90.0		139.0	1.10	109.0		30.3	1.40	60.0	1.06
97.6	200.5		91.0		138.5	1.41	109.5		29.0		62.0	
98.5	201.0		91.0		138.0		109.0		29.0		63.0	
101.0	201.5		92.0		138.0		109.0		29.5		63.0	
101.0	201.5		92.0		138.0		109.0		29.5		63.0	

ᵃ α(alkyl)–β(alkyl). ᵇ β(acyl)–α(alkyl). ᶜ α(acyl)–β(alkyl). ᵈ β(acyl)–β(alkyl). ᵉ β(acyl)–α(acyl). ᶠ α(acyl)–α(alkyl).

Table III. A Comparison of Results Obtained Using All Possible Chemical Shift Differences of Ethyl 3-Chloropropionate
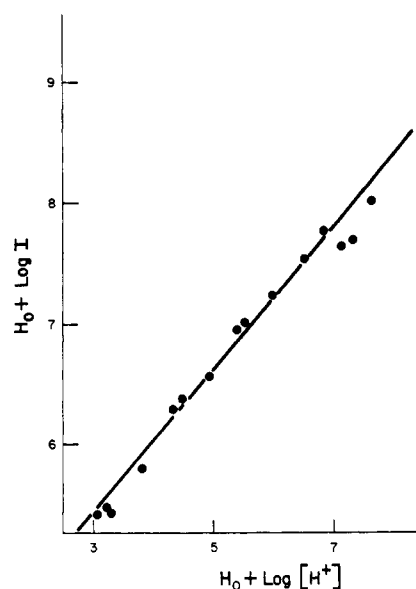
Chemical shift	Δ_BH⁺, Hz	Δ_B, Hz	Log I vs. −H₀ plot Slope	Log I vs. −H₀ plot Intercept	Log I vs. −H_E plot Slope	Log I vs. −H_E plot Intercept
α(alkyl)–β(alkyl)	201.00	177.5	0.61 ± 0.07	−8.2 ± 0.1	0.98 ± 0.06	−4.0 ± 0.1
α(acyl)–α(alkyl)	63.0	25.5	0.57 ± 0.03	−8.2 ± 0.1	0.88 ± 0.04	−4.0 ± 0.1
β(acyl)–α(alkyl)	91.0	81.0	0.57 ± 0.10	−8.2 ± 0.2	0.87 ± 0.12	−4.0 ± 0.1
α(acyl)–β(alkyl)	138.5	151.0	0.62 ± 0.06	−8.4 ± 0.2	0.90 ± 0.16	−4.0 ± 0.2
β(acyl)–α(acyl)	29.0	55.0	0.61 ± 0.07	−8.2 ± 0.1	0.96 ± 0.07	−4.0 ± 0.1
β(acyl)–β(alkyl)	109.5	97.0	0.77 ± 0.15	−8.2 ± 0.2	0.97 ± 0.09	−3.9 ± 0.1
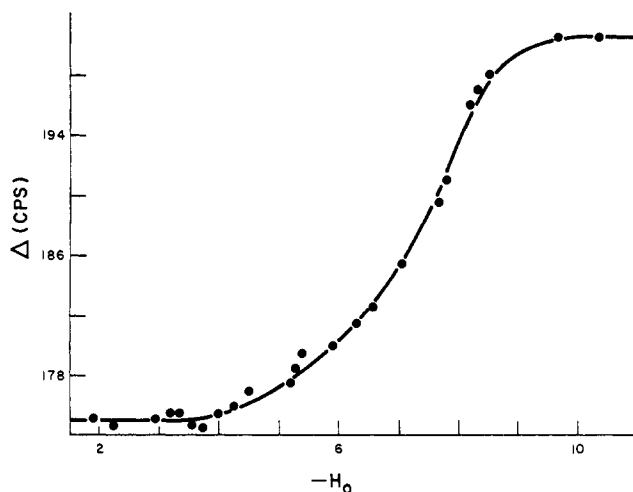
Figure 1. Titration curve for the protonation of ethyl acetate.

Figure 2. Bunnett–Olsen plot for ethyl acetate.

ical shifts of the α and β hydrogens of the alkyl group whenever possible.

Results and Discussion

As shown in Figure 1 the plot of Δ (the difference between the chemical shifts of the α- and β-alkyl hydrogens in ethyl acetate) against H_0 gives a sigmoidal curve, thus indicating that the spectral shifts are due to protonation of the ester. The Bunnett–Olsen plot (Figure 2) obtained from an analysis of the data gives a pK_{BH^+} value of −3.45 ± 0.17 for ethyl acetate. Since we intended to use this value for subsequent establishment of an ester acidity function it was important to test the

validity of this value as thoroughly as possible. Hence, two methods of verification were attempted. First of all, the ultraviolet absorption data which are available in the literature[9] were also subjected to a Bunnett–Olsen analysis. Although the values of I are dependent on the wavelength used to estimate the extent of protonation, it is evident from the results presented in Table IV that the basicity constants are close to the values obtained by nmr measurements. Secondly, it was ob-
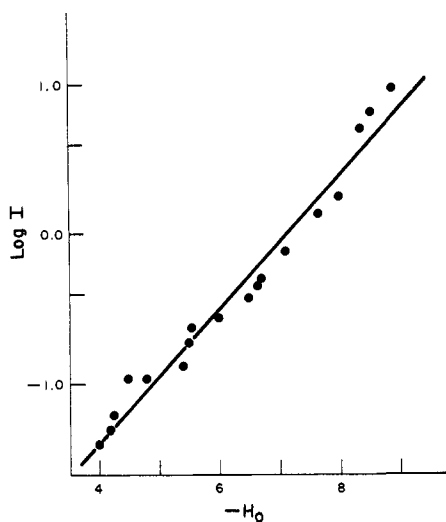
Figure 3. Plot of log I against H_0 for ethyl acetate.

Table IV. Calculated pK_{BH^+} Values for Ethyl Acetate Using the Uv-Spectral Data Reported by Siigur and Haldna[9]

Wave-length, nm	Bunnett-Olsen plots		—Log I vs. $-H_0$ plots—		
	Slope	pK_{BH^+}	Slope	Intercept	pK_{BH^+}
186.9	0.58	−3.21	0.47	−6.10	−2.86
190.5	0.59	−3.22	0.44	−6.36	−2.79
192.3	0.50	−3.52	0.54	−6.07	−3.27
204.1	0.51	−3.57	0.53	−6.13	−3.20
206.2	0.50	−3.43	0.54	−5.79	−3.10

served that if a plot of log I vs. $-H_0$ was prepared (Figure 3) a straight line with a slope of 0.51 ± 0.04 and an intercept of −7.1 ± 0.1 was obtained. From this it can be calculated, assuming a linearity between H_0 and H_E, that the pK_{BH^+} of ethyl acetate should be −3.6 ± 0.3. A similar analysis of the ultraviolet data of Siigur and Haldna[9] gave a value of −3.1 ± 0.3. On the basis of these results it would appear that a value of −3.45 for the pK_{BH^+} of ethyl acetate is not unreasonable.

Accepting this value for the basicity constant of ethyl acetate the data in Table I were applied to eq 4, thus defining an ester acidity function (H_E) between 60 and 88% H_2SO_4. Following this it was possible to use ethyl 3-chloropropionate, since it overlaps well with ethyl acetate (Figure 4), as an indicator to extend the function to 98% H_2SO_4. The values of H_E obtained by drawing a smooth line through the experimental points have been summarized in Table V.

Table V. The H_E Function

H_2SO_4, %	H_E	H_2SO_4, %	H_E
60	−2.2	85	−4.0
65	−2.5	90	−4.6
70	−2.8	95	−5.2
75	−3.1	98	−5.5
80	−3.5		

Having established an ester acidity function in the region of interest it was then possible to analyze the data obtained from a variety of esters in three different ways using eq 2–4. The results obtained for several
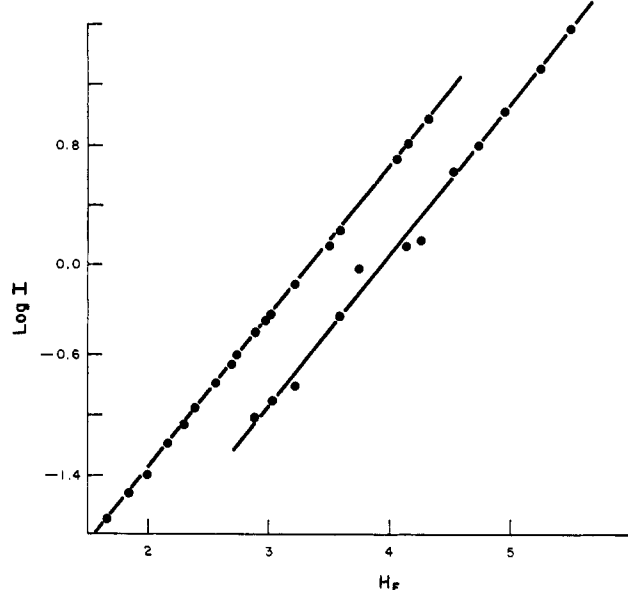

Figure 4. Plot of log I against H_E for ethyl acetate (top) and ethyl 3-chloropropionate (bottom).

unsubstituted aliphatic esters are given in Table VI, and a number of observations can be made on the basis of these data. It is apparent that all of the methods give basicity constants that are in the majority of cases within experimental error of each other. There seems to be little doubt that these results give pK_{BH^+} values which may be used with some confidence. However, it should be noted that the slopes of the plots of log I vs. $-H_0$ are, with one exception, smaller than the value of 0.62 reported by Yates and McClelland[8] and Lane[7] on the basis of ultraviolet spectroscopic data. Also, the slopes of the plots of log I vs. $-H_E$ are not all unity, thus suggesting that the protonation behavior of each ester is unique, a possibility that is further emphasized below.

Siigur and Haldna[9] have previously reported ultraviolet spectral data which also permit the calculation of basicity constants for several aliphatic esters by application of eq 2–4. The careful work of these authors indicated that the results were somewhat dependent on the wavelength at which the study was completed and they consequently attempted to minimize deviations by averaging over two or three wavelengths. In Table VII we have taken the liberty of summarizing the results which are obtained if their data are analyzed in each of the three approaches described above. It is quite evident by a comparison of Tables VI and VII that similar conclusions are arrived at from the use of either nmr or uv spectral data to estimate the extent of protonation.

Next it is instructive to note what happens when substituents are introduced into the structure of aliphatic esters. Table VIII contains a summary of the results, which we have obtained from such a study. Since most of these compounds are too weakly basic to be significantly protonated below 85% H_2SO_4, a Bunnett–Olsen analysis could not be attempted; however, the agreement between the pK_{BH^+} values obtained from use of both the H_0 and the H_E scales is in most cases satisfactory. Furthermore, for those two esters (ethyl chloroacetate and ethyl 3-chloropropionate) which were

Table VI. Basicity Constants for Unsubstituted Aliphatic Esters

Ester	Bunnett–Olsen plots		Log I vs. $-H_0$ plots			Log I vs. $-H_E$ plots		
	Slope	pK_{BH}^{+a}	Slope	Intercept	pK_{BH}^{+b}	Slope	Intercept	pK_{BH}^{+c}
Ethyl acetate	0.63 ± 0.03	-3.45 ± 0.17	0.51 ± 0.04	-7.1 ± 0.1	-3.6 ± 0.3^d	1.00 ± 0.01	-3.5 ± 0.2	-3.5 ± 0.2
n-Propyl acetate	0.43 ± 0.06	-4.6 ± 0.4^d	0.68 ± 0.08	-7.2 ± 0.1	-4.8 ± 0.3	1.3 ± 0.1	-3.4 ± 0.1	-4.3 ± 0.3
Ethyl propionate	0.53 ± 0.04	-4.1 ± 0.2^e	0.57 ± 0.04	-7.2 ± 0.1	-4.1 ± 0.3	1.1 ± 0.2	-3.4 ± 0.1	-3.6 ± 0.5
Isopropyl acetate	0.52 ± 0.03	-3.6 ± 0.1^e	0.51 ± 0.03	-6.3 ± 0.1	-3.2 ± 0.2^e	1.2 ± 0.1	-3.0 ± 0.1	-3.5 ± 0.2^f
n-Butyl acetate	0.51 ± 0.03	-4.1 ± 0.2	0.54 ± 0.03	-7.1 ± 0.1	-3.8 ± 0.2	1.0 ± 0.1	-3.5 ± 0.1	-3.5 ± 0.2
Isobutyl acetate	0.54 ± 0.03	-4.0 ± 0.2	0.54 ± 0.03	-7.1 ± 0.1	-3.8 ± 0.2	1.0 ± 0.1	-3.5 ± 0.1	-3.5 ± 0.3

[a] Intercept of a plot of $H_0 + \log I$ vs. $H_0 + \log [H^+]$ (correlation coefficients greater than 0.98 unless noted). [b] Product of slope $\times$ intercept for plots of $\log I$ vs. H_0 (correlation coefficients greater than 0.98 unless noted). [c] Product of slope $\times$ intercept for plots of $\log I$ vs. H_E (correlation coefficients greater than 0.98 unless noted). [d] Correlation coefficient $= 0.96$. [e] Correlation coefficient $= 0.95$. [f] Correlation coefficient $= 0.94$.

Table VII. Basicity Constants for Aliphatic Esters Calculated from Uv-Spectral Data[a]

Ester	λ, nm[b]	Bunnett–Olsen plots		Log I vs. $-H_0$ plots			Log I vs. $-H_E$ plots		
		Slope	pK_{BH}^{+}	Slope	Intercept	pK_{BH}^{+}	Slope	Intercept	pK_{BH}^{+}
Ethyl acetate	186.9, 190.5, 192.5	0.56	-3.3	0.47	-6.2	-2.9	0.90	-2.9	-2.6
Ethyl acetate	204.1, 206.2	0.50	-3.5^d	0.53	-6.0	-3.2^c	0.98	-2.8	-2.8^d
Ethyl propionate	190.5, 192.3, 194.2	0.53	-3.8^d	0.53	-6.7	-3.5	1.1	-3.2	-3.6
Ethyl propionate	204.1, 206.2	0.49	-3.9	0.53	-6.5	-3.4	1.1	-3.1	-3.4
n-Butyl acetate	188.7, 190.5, 192.3	0.46	-4.1	0.55	-6.6	-3.6	1.2	-3.1	-3.6
Methyl propionate	188.7, 190.5	0.62	-3.3	0.50	-6.8	-3.1	0.96	-3.2	-3.1
Methyl propionate	200.0, 202.0	0.66	-3.4^d	0.52	-7.2	-3.8^d	1.0	-3.5	-3.5^c
Ethyl butyrate	189.9, 190.5, 194.2	0.52	-4.0	0.59	-7.0	-4.1	1.1	-3.3	-3.7
Ethyl α-methylbutyrate	186.9, 190.5, 194.2	0.55	-4.0	0.53	-7.4	-3.9	0.82	-3.6	-2.9^c
Ethyl chloroacetate	190.5, 194.2, 198.0			0.51	-9.8	-5.0	0.78	-5.1	-4.0
Ethyl 3-chloropropionate	190.5, 192.3, 196.1			0.47	-8.3	-3.9	0.71	-4.1	-2.9
Ethyl benzoate	195.0, 230.0, 260.0	0.39	-8.2^c	0.75	-8.0	-6.0^c	1.1	-3.9	-4.1^c

[a] The spectral data on which these calculations are based have been reported by Siigur and Haldna.[9] All plots have correlation coefficients of 0.95 or greater unless otherwise noted. [b] The wavelength at which the data were obtained. In each case readings from two or three wavelengths were averaged.[9] [c] Correlation coefficients between 0.90 and 0.94. [d] Correlation coefficient less than 0.90.

Table VIII. Basicity Constants for Substituted Aliphatic Esters[a]

Ester	Bunnett–Olsen plots		Log I vs. $-H_0$ plots			Log I vs. $-H_E$ plots		
	Slope	pK_{BH}^{+}	Slope	Intercept	pK_{BH}^{+}	Slope	Intercept	pK_{BH}^{+}
Ethyl chloroacetate	b	b	0.62 ± 0.08	-9.5 ± 0.2	-5.9 ± 0.8	0.85 ± 0.11	-4.9 ± 0.1	-4.2 ± 0.5
Ethyl 3-chloropropionate	b	b	0.61 ± 0.07	-8.2 ± 0.1	-5.0 ± 0.6	0.98 ± 0.12	-4.0 ± 0.2	-4.0 ± 0.5
Ethyl cyanoacetate	b	b	0.38 ± 0.15	-9.2 ± 0.3	-3.4 ± 1.4^d	0.51 ± 0.21	-4.7 ± 0.5	-2.4 ± 1.0^d
Ethyl acetoacetate	0.67 ± 0.05	-3.7 ± 0.3	0.52 ± 0.04	-8.4 ± 0.1	-4.3 ± 0.3	0.78 ± 0.06	-4.1 ± 0.1	-3.2 ± 0.2
Ethyl 2-chloroacetoacetate	0.80 ± 0.08	-2.3 ± 0.5	0.27 ± 0.07	-7.1 ± 0.7	-1.9 ± 0.6^c	0.50 ± 0.16	-3.4 ± 0.4	-1.7 ± 0.5
Ethyl crotonate	0.44 ± 0.05	-4.2 ± 0.3	0.59 ± 0.04	-6.6 ± 0.1	-3.9 ± 0.3	1.3 ± 0.3	-3.2 ± 0.1	-4.1 ± 0.8
Ethyl phenylacetate	b	b	0.83 ± 0.09	-8.1 ± 0.1	-6.7 ± 0.7	1.31 ± 0.1	-3.9 ± 0.1	-5.0 ± 0.5
Ethyl benzoate	b	b	1.3 ± 0.2	-8.2 ± 0.1	-11 ± 2^d	1.8 ± 0.3	-4.0 ± 0.1	-7.3 ± 1.1

[a] All plots have correlation coefficients of 0.95 or greater unless otherwise noted. [b] Bunnett–Olsen plots could not be obtained because the esters were not appreciably protonated below 85% H_2SO_4. [c] Correlation coefficient $= 0.94$. [d] Correlation coefficient $= 0.93$. [e] Correlation coefficient $= 0.92$.

also studied by Siigur and Haldna,[9] the agreement between our work and theirs is good.

It is quite evident that the protonation behavior of those esters bearing substituents which are very near to the site of protonation or conjugated with it cannot be adequately described by the H_E function; in very few cases are the slopes of the $\log I$ vs. $-H_E$ plots close to unity. This simply means that each of these esters responds in an individual way while undergoing protonation, and thus suggests the probability that it will not be possible to develop a universally acceptable acidity function for any but the unsubstituted esters.

The difficulties with substituted esters are probably related to the fact that substituents not only change the electronic character of the molecule but also its solvation properties. It is known, for example, that compounds which form conjugate acids with high solvation requirements undergo protonation less readily as the

acidity of a solution is increased. The reason for this lies in the fact that an increase in acidity also results in a decrease in the amount of water available for solvation and conjugate acids with high solvation requirements will consequently be formed less readily.

The most apparent indication of solvation requirements is the slope of plots of log I vs. $-H_0$. Compounds which form conjugate acids having lower solvation requirements than protonated anilines exhibit slopes greater than unity. For example, triphenylcarbinols which form carbonium ions on protonation give slopes of about 2 because such ions are not readily solvated by water.[10] On the other hand, the oxonium ion which forms when ethanol is protonated must be highly solvated and a slope of 0.25 is obtained.[4]

A similar tendency can be noted among the esters studied in this investigation. Compare, for example, ethyl acetate with phenylethyl acetate and ethyl benzoate. Of these three compounds, the conjugate acid which forms when ethyl acetate is protonated would be expected to have the greatest solvation requirements because the positive charge will be localized primarily on the two oxygen atoms. On the other hand, the charge on the conjugate acid of ethyl benzoate could be

delocalized over the aromatic ring as well as on the two oxygens. Consequently, its requirement for solvation is much less and the slope much greater, being 1.3 for ethyl benzoate as compared to 0.51 for ethyl acetate, with phenylethyl acetate (where only partial delocalization is possible) having an intermediate value of 0.83.

In conclusion, it can be seen that the problem of determining quantitatively the basicity constants for aliphatic esters, particularly those with complex structures, may not be easily solved; each particular compound may have to be independently investigated. It can also be seen that aliphatic and aromatic esters do not conform to the same acidity functions. On the other hand, the protonation behavior of several simple unsubstituted aliphatic esters appears to be satisfactorily defined by the H_E function.

Radicals and Scavengers. V. Steric Hindrance and Cage Effects in the Decompositions of Several *tert*-Butyl Peresters[1a]

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Abstract: Product isolation and scavenger methods have been used to study the cage effects in decompositions in cumene and chlorobenzene of several *tert*-butyl peresters, RCO_3-*t*-Bu, including the peracetate (I, R = CH_3), perpivalate (II, R = $(CH_3)_3C$), *p*-nitro- and *p*-methoxyphenylperacetates (III and IV, R = p-$O_2NC_6H_4CH_2$ and p-H_3C-$OC_6H_4CH_2$, respectively), α-phenylperisobutyrate (V, R = $C_6H_5C(CH_2)_3$), α,α-diphenylperpropionate (VII, R = $(C_6H_5)_2C(CH_3)$), and diphenylpermalonate (IX, $(C_6H_5)_2C(CO_3$-*t*-Bu$)_2$). As previously reported for the diphenylperacetate (VI, R = $(C_6H_5)_2CH$), reaction of *tert*-butoxy radicals with R· in bulk solution does not occur. For tertiary R, cage effects involving coupling are small, *ca.* 0–12%, but for primary R, *ca.* 30% or more. Disproportionation is *ca.* 5–10% per β-hydrogen atom of R. Steric repulsion is proposed as explanation for small or nil amounts of cage coupling.

$\mathbf{T}$he *tert*-butyl peresters are interesting initiators for studies of the cage effect, the mutual reaction of geminate radical in solution.[2] Since the *tert*-butoxy radical is formed by all homolytic decompositions of *tert*-butyl peresters,[3] the series presents an opportunity to study a structure–reactivity relationship.

We have carried out a series of scavenger studies of the thermal decompositions of II, IV, V, and VII, and product studies with I–V, VII, and IX, which supplement the studies of IV and its analogs,[4] V,[5] VI,[1,6] VIII,[1]

and X[7] already reported. Scavenger studies of XI[8] and XII[9] have also been reported, as have photolytic studies of I, II, and an extensive series of their aliphatic analogs at 30°, and the thermolysis of I in decalin at 115°.[10] Data are therefore at hand for primary, secondary, and tertiary alkyl and aralkyl radicals between 25 and 115°.

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