

Basicities of the Oxygen Atoms in Symmetrical and Unsymmetrical Acetals. Part I. The Determination of Base Strengths by Infrared Spectroscopy

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The basicities of sixteen acetals of formaldehyde (dialkoxy-methanes) $R_nOCH_2OR_m$ with different alkyl groups (CH_3 , CH_3CH_2 , $(CH_3)_2CH$, $(CH_3)_3C$, $ClCH_2CH_2$, FCH_2CH_2 , Cl_3CCH_2 , F_3CCH_2 , and C_6H_5) were determined by a spectral shift method. The validity of this method was checked by measuring the O-D band shifts for methanol- d_1 in ethers whose basicities are known. The pK_a values of the protonated forms of the different oxygen atoms in acetals were calculated from the measured basicities.

In a previous study, Salomaa¹ determined the contributions of different fission reactions in the hydrolysis of unsymmetrical and symmetrical acetals. These partial rate coefficients are products of two factors; the equilibrium constant of the protonation and the rate coefficient of unimolecular decomposition of the protonated substrate. To determine the effects of these two factors on the partial rates, the basicities of both oxygen atoms of the acetal must be known.

Because acetals are readily hydrolyzed, their pK_a values cannot be measured in strong aqueous acids. It has previously been found, however, that a number of organic bases influence the stretching frequency of the bond of the acidic hydrogen in deuteromethanol.² Because the magnitude of this effect has been shown to be proportional to the pK_a value of the solvent, the hydrogen bond shift method was applied to determine the basicities of acetals.

EXPERIMENTAL

Materials. Most of the dialkoxy-methanes studied in this work were those previously prepared in this laboratory by Salomaa.¹ The fractions which were used for the pK_a measurements were purified by distillation from metallic sodium. The purities of these fractions were checked by gas chromatography. Di- β,β,β -trichloroethoxymethane and

isopropoxy- β,β,β -trichloroethoxymethane were those prepared by Salomaa and Linnantie.³ The syntheses of di- β,β,β -trifluoroethoxymethane and diphenoxymethane were carried out in a recent work.⁴

Most of the ethers used as standard liquids in the pK_a measurements were commercial products which were purified by distillation from metallic sodium. *sec*-Butyl phenyl ether and *o*-methoxytoluene were prepared by standard methods.⁵ *sec*-Butyl phenyl ether: b.p. 84–86°C/18 torr and n_D^{20} 1.4941. *o*-Methoxytoluene: b.p. 172–173°C/760 torr and n_D^{20} 1.5172. The purities of the ethers were checked by gas chromatography.

IR measurements. The used apparatus was a Perkin Elmer grating infrared spectrometer connected to a Honeywell continuous balance potentiometer to broaden the spectrum. A sodium chloride cell was used. The thickness of the liquid layer was 0.1 mm. The temperature during the measurements was about 25°C. The possible small variations in temperature did not alter the band shifts within the limits of experimental error as shown by experiments conducted at temperatures between 10 and 50°C.

About 10 μ l of methanol- d_1 was added to 0.5 ml of acetal to give an approximately 0.5 M solution. The reference cell was filled with the solvent. Each measurement was repeated 5–10 times and the relative standard errors (less than 0.03 %) were calculated. The bands of polystyrene (2850.7, 1944.4 and 1601.4 cm^{-1}) were used as standards from which the frequencies of the O–D bands were measured.

RESULTS AND DISCUSSION

Spectral results. The pK_a values of only a few acetals have previously been measured.^{6,7} Therefore ethers which are alkyl-substituted oxygen bases like acetals, were chosen as standard substances to evaluate the pK_a values from the O–D band shifts. The nine ethers listed in Table 1, whose pK_a

Table 1. O–D band shifts of methanol- d_1 in different ethers, the pK_a values of which have been measured previously by other methods. 25°C.

Compound	$-pK_a^2$	Position of O–D band (cm^{-1}) ^a	O–D band shift (cm^{-1})
Tetrahydrofuran	2.08	2577.9 \pm 1.1	112.0
Di-butyl ether	3.05 ⁸	2590.8 \pm 0.4	99.1
1,4-Dioxane	3.22	2591.8 \pm 0.3	98.1
1,2-Dimethoxyethane	3.27	2596.7 \pm 0.3	93.2
Diethyl ether	3.59	2593.2 \pm 0.5	96.7
<i>sec</i> -Butyl phenyl ether	5.36	2622.4 \pm 0.4	67.5
<i>o</i> -Methoxytoluene	5.87	2629.5 \pm 0.4	60.4
Ethoxybenzene	6.44	2629.1 \pm 0.4	60.8
Methoxybenzene	6.54	2632.6 \pm 1.0	57.3

^a Frequency of O–D band in carbon tetrachloride 2689.9 \pm 0.5 cm^{-1} .

values vary between 2 and 6.5, were studied. When the measured band shifts are plotted against the pK_a values given by Arnett,² a linear plot is obtained (Fig. 1); the pK_a value determined by Fomin and Maslova⁸ was used for dibutyl ether. A straight line was fitted by the method of least squares (eqn. 1).

$$pK_a = (0.0789 \pm 0.0042)\Delta\nu - (10.91 \pm 0.34) \quad (1)$$

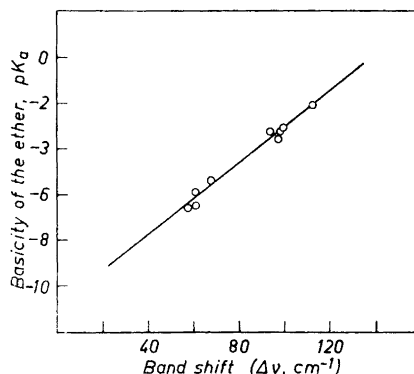


Fig. 1. The relationship between the basicity of the solvent and the O—D band shift of methanol- d_1 in different solvents of the ether type ROR'.

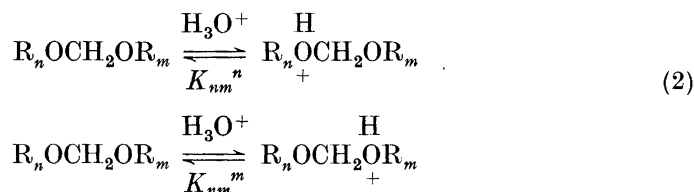
The spectral data for the studied dialkoxymethanes are collected in Table 2 together with the pK_a values calculated from eqn. (1). A variation of about 5 pK_a units is found for the studied acetals. The maximum relative errors of these pK_a values calculated from the standard errors of eqn. (1)

Table 2. O—D band shifts of methanol- d_1 in different acetals $R_nOCH_2OR_m$ and pK_a values of the conjugate acids of these acetals at 25°C.

R_n	Substituents R_m	O—D band position (cm^{-1})	Band shift (cm^{-1})	$-pK_a$	Ref.
CH_3	CH_3	2609.5 ± 0.8	80.4	4.57	This work
CH_3CH_2	CH_3CH_2	2604.0 ± 0.5	85.9	4.13	» »
$(CH_3)_2CH$	$(CH_3)_2CH$	2598.5 ± 0.5	91.4	3.70	» »
$(CH_3)_3C$	$(CH_3)_3C$	2587.7 ± 0.2	102.2	2.85	» »
FCH_2CH_2	FCH_2CH_2	2614.9 ± 0.7	75.0	4.99	» »
$ClCH_2CH_2$	$ClCH_2CH_2$	2619.0 ± 0.4	70.9	5.32	» »
F_3CCH_2	F_3CCH_2	2658.1 ± 0.2	31.8	8.40	4
Cl_3CCH_2	Cl_3CCH_2	2651.1 ± 0.3	38.8	7.85	»
C_6H_5	C_6H_5	2631.7 ± 0.2	58.2	6.53	»
CH_3	CH_3CH_2	2606.1 ± 0.5	83.8	4.30	This work
CH_3	$(CH_3)_2CH$	2602.5 ± 0.4	87.4	4.01	» »
CH_3	$ClCH_2CH_2$	2609.6 ± 0.3	80.3	4.57	» »
CH_3CH_2	$ClCH_2CH_2$	2607.3 ± 0.3	82.6	4.39	» »
CH_3CH_2	$(CH_3)_2CH$	2603.4 ± 0.4	87.3	4.02	» »
$(CH_3)_2CH$	$ClCH_2CH_2$	2602.1 ± 0.5	87.8	3.98	» »
$(CH_3)_2CH$	Cl_3CCH_2	2606.5 ± 0.5	83.4	4.33	» »

are about 10 %. As the basicities of the studied acetals are compared with each other, the errors of these differences are much smaller than those of the pK values themselves as a result of the similar structures of the studied compounds. Fairly good estimates of these errors can be obtained on the basis of the standard errors of the measured band shifts. Relative errors less than three per cent are obtained in this way.

Dissection of the basicities of the acetals. The basicities of the oxygen atoms in acetals $R_nOCH_2OR_m$ can be calculated on the basis of the measured pK_a values. Let us denote by K_{nm}^n and K_{nm}^m the different equilibrium constants:



The lower index pair refers to the substituents R_n and R_m of the acetal and the upper index to the site of protonation in question. We can assume that the alkyl group R which is not directly attached to the oxygen atom whose protonation is being discussed has only a negligible influence on the basicity of this hetero atom owing to the long distance. This assumption is reasonable on the basis of Taft's σ^* values of different substituents. The polar constants of, *e.g.*, methyl and hydrogen differ about 0.50 units, but the inductive effects of these substituents decrease markedly with the distance as can be seen from the nearly equal σ^* values of the groups CH_3OCH_2- and $HOCH_2-$.⁹ Thus

$$pK_{nm}^n = pK^n \quad (3)$$

The overall equilibrium constant measured for an unsymmetrical acetal can be expressed in the form:

$$1/K_{nm} = 1/K^n + 1/K^m \quad (4)$$

For a symmetrical acetal, the basicities of both oxygen atoms are naturally equal and thus

$$1/K_{nm} = 2/K^n \quad (n=m) \quad (5)$$

In pK units

$$pK^n = pK_{nm} - \log 2 \quad (5')$$

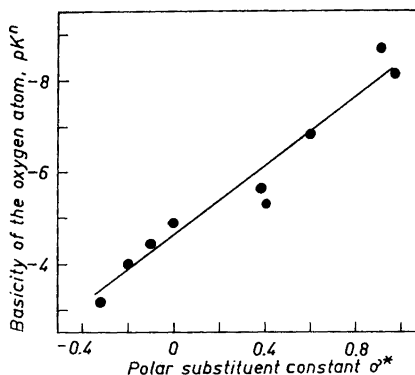
When the pK values of the symmetrical acetals in Table 2 are substituted into this equation, the following basicities of the different oxygen atoms are obtained:

$R_n = R_m$	CH_3	CH_3CH_2	$(CH_3)_2CH$	$(CH_3)_3C$	FCH_2CH_2	$ClCH_2CH_2$	F_3CCH_2	Cl_3CCH_2	C_6H_5
pK^n	-4.87	-4.43	-4.00	-3.15	-5.29	-5.62	-8.70	-8.15	-6.83

When these pK^n values are plotted against Taft's σ^* values for alkyl groups, a linear relationship is found (Fig. 2) between the basicity of an oxygen atom and the electron-releasing or electron-attracting power of the substituent attached directly to this oxygen atom.

To evaluate the validity of eqn. (3), the overall pK values of the unsymmetrical acetals studied in this work were calculated from eqn. (4) and are compared below with the experimental basicities:

Fig. 2. The relationship between the basicity of the oxygen atom and the polar substituent constant σ^* of the neighbouring alkyl group for acetals of formaldehyde. The σ^* values of β -fluoroethyl and β, β, β -trichloroethyl have been estimated by a previously described method.¹⁰



R_n	CH_3	CH_3	CH_3	CH_3CH_2	CH_3CH_2	$(CH_3)_2CH$	$(CH_3)_2CH$
R_m	CH_3CH_2	$(CH_3)_2CH$	$ClCH_2CH_2$	$(CH_3)_2CH$	$ClCH_2CH_2$	$ClCH_2CH_2$	Cl_3CCH_2
pK (calc.)	-4.30	-3.95	-4.80	-3.86	-4.40	-3.99	-4.00
pK (obs.)	-4.30	-4.01	-4.57	-4.02	-4.39	-3.98	-4.33

It is seen that these values are equal within the limits of experimental error.

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