constant. If this hypothesis is valid, a plot of the enthalpy of formation (ΔH) *versus* $\Delta \nu$ should give a linear plot including all the sulphoxides. This will be discussed in some more detail in a forthcoming paper [10] on the phosphine oxide-iodine cyanide complexes.

In an earlier paper [8] the hydrogen bond between phenol and various sulphoxides were studied and correlated with the spectral parameters in the $O-H$ stretching region. For these systems linear relationships were obtained when $\Delta \nu_{O-H}$ was plotted against log K, $-\Delta G$, $-\Delta H$, and $-\Delta S$. Moreover, the relative frequency shifts $(\Delta \nu/\nu)_{C-I}$ and $(\Delta \nu/\nu)_{O-H}$ for the same sulphoxide show a parallel behaviour. Thus, inside the error limits, the ratio $(\Delta \nu/\nu)_{C-I}/(\Delta \nu/\nu)_{O-H}$ is constant for each sulphoxide, supporting the close relationship between the charge transfer and the hydrogen bonds.

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The Hydrolysis of 1,3-Dioxane and Its Derivatives

## Part I. The Position of the Equilibrium and the Formal Kinetic Laws

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1,3-Dioxane and its derivatives are acetals and are thus readily hydrolyzed in acidic media. The present paper reports some general observations made in kinetic studies of the reaction.

The hydrolysis was studied in dilute hydrochloric acid solutions. It was found that the formal rate laws and the position of the equilibrium of the hydrolysis reaction differed markedly from those of related compounds, 1,3-dioxolanes.[1] In the case of 1,3-dioxane and its derivatives the equilibria were incompletely on the side of the reaction products. This observation is in qualitative agreement with that of Aftalion *et al.*[2,3] However, the latter authors did not pay attention to the presence of semiacetals in the equilibria involved.

The equilibrium position was described by Aftalion *et al.* [2,3] as follows

$$A + 2 H_2O \xrightleftharpoons{K_c} C + G, \qquad (1)$$
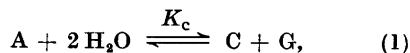
where $K_c = [C][G]/[A][H_2O]^2$

(A = 1,3-dioxane, C = aldehyde and G = diol), in which [C] and [G] were calculated from the amount of A reacted. Taking into account that semiacetal is a reaction intermediate the equilibria are the following (neglecting, for simplicity, the constant amount of water present):

$$A \xrightleftharpoons{K_1} S \xrightleftharpoons{K_2} C + G, \text{ where } K_1 = [S]/[A]$$

and $K_2 = [C][G]/[S]$, S = semiacetal). (2)
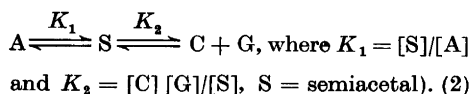
Let us denote

$$K' = ([S] + [C])/[A] \qquad (3)$$

K' relates to the apparent equilibrium position, where $[S] + [C]$ is directly obtained from the amount of A reacted.

Table 1. The equilibrium constants for the hydrolysis of 2-methyl-1,3-dioxane at 45°C. $[A]_0$ = the initial concentration of 2-methyl-1,3-dioxane, $[G]_0$ = the initial concentration of 1,3-propane-diol, $[S] + [C]$ = the concentration of the dioxane reacted at equilibrium, $[A]$ = the concentration of the unreacted dioxane. (All concentrations in mole/litre).

$[A]_0$	$[G]_0$	$[S] + [C]$	$[A]$	K'	K_1	K_2 mole/l
0.1064	0.00000	0.0821	0.0243	3.38		0.295
0.1062	0.02678	0.0779	0.0284	2.75		0.295
0.1058	0.05308	0.0740	0.0318	2.33	0.625	0.292
0.1057	0.06241	0.0730	0.0327	2.24		0.296
0.1055	0.08800	0.0699	0.0356	1.97		0.292

Mean	0.294

For calculating the equilibrium constants K_1 and K_2 the following expression is obtained from eqns. (2) and (3)
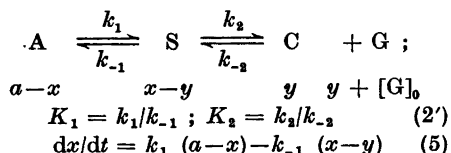
$$K' = K_1 + (K_1 K_2/[G]) \qquad (4)$$

where $[G] = [S] + [C] - [S] + [G]_0$; $[G]_0$ = the initial diol concentration.

The results of a number of measurements are recorded in Table 1. The results show that the semiacetal concentration at equilibrium is fairly large. At lower temperatures the significance of the semiacetal was found to be even greater as the values of K' were decreasing.

The equilibrium constant K_c adopted by Aftalion *et al.* [2,3] seems to remain virtually constant only when the equilibrium is completely on the side of the reaction products, or, when the initial diol concentration is relatively large, *i.e.*, in cases in which the aldehyde-semiacetal equilibrium is practically completely on either side.

In the kinetic experiments it was found that the hydrolysis of 1,3-dioxanes proceeded according to the reaction scheme (2') and followed the rate law (5)

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C + G ;$$

$$a - x \qquad x - y \qquad y \qquad y + [G]_0$$

$$K_1 = k_1/k_{-1} ; \quad K_2 = k_2/k_{-2} \qquad (2')$$

$$dx/dt = k_1 (a - x) - k_{-1} (x - y) \qquad (5)$$

Here a denotes the initial dioxane concentration, x the concentration of dioxane reacted in time t, y the concentration of aldehyde formed in time t, k_1 the rate coefficient of the hydrolysis reaction and k_{-1} the rate coefficient of the acetalization reaction.

Table 2. The rate coefficients of the hydrolysis of 2-methyl-1,3-dioxane at 45°C. $[G]_0$ is the initial concentration of 1,3-propanediol (mole/l), $[A]_0$ the initial concentration of 2-methyl-1,3-dioxane (mole/l), h the concentration of the catalyst hydrochloric acid (mole/l), and k_a is the apparent overall rate coefficient $(l/mole^{-1}s^{-1})$.

$[G]_0$	$[A]_0$	h	$10^2 k_a$	$10^2 k_1$ l mole^{-1}s^{-1}
0.0000	0.107	0.0981	5.65	4.35
0.0274	0.106	0.0979	5.89	4.32
0.0501	0.106	0.0977	6.13	4.43
0.0789	0.106	0.0975	6.30	4.22
0.1056	0.106	0.0973	6.70	4.30

Mean	4.32

Table 2 gives the results obtained in a set of kinetic experiments. It is seen that the agreement between the rate coefficients is very good, taking into account that the initial conditions were different.

2-Methyl-1,3-dioxane was prepared by a method described by Rondestvedt, Jr.[4] It was purified carefully by distilling in a Todd assembly. B.p. 108—111 °C/763 mm Hg, n_D^{20}- = 1.4133, d_4^{20} = 0.9673, $(R_D)_{obs}$ = 26.30 and $(R_D)_{calc}$ = 26.28.

The modification of the bisulphite method described by Salomaa [5] was used for determining the concentration of the reacted dioxane.

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Preparation of 300—500 mg Quantities of Isotopic Methyl Ketenes

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Methyl-[1-^{13}C] ketene. 20 mmole ^{13}C-enriched CO_2 (from 4 g 55 % enriched $BaCO_3$(= Ba*CO_3)) was distilled into a cooled ($-70°C$) Grignard solution prepared from 30 mmole ethyl bromide (3.2 g), 0.85 g Mg and 0.4 g I_2 in 50 ml ether. Afterwards, over a period of 1 h, the temperature was raised to $-20°C$. In 10 min, 50 ml water was added, the temperature rising to 0°C. After filtering, CH_3CH_2*COOH was neutralized by 50 ml 2N NaOH in the combined water and ether phases and the ether phase discarded. 7 g Ag_2SO_4 with 100 ml water was added to the aqueous phase for precipitation of AgBr and AgI. 300 ml water was distilled-off at 100°C while an equal quantity of water was simultaneously added. 50 ml half-concentrated H_2SO_4 was added to the distillation flask, liberating CH_3CH_2*COOH, which was distilled-off at 100°C with 800 ml water, which was replaced during the distillation as above. Titration of the aqueous distillate (I) showed that it contained 19.8 mmole acid. After neutralization, water was evaporated from one-half part of (I), and 15 ml phthaloylchloride was added. The flask was connected to a reflux condenser, heated to $175-180°C$ for 1 h and cooled. CH_3CH_2*COCl was separated from the reaction mixture by distillation in a high vacuum, the temperature of the bath surrounding the flask being gradually raised from 25°C to 60°C. By a following single-plate distillation *in vacuo*, 9.7 mmole of CH_3CH_2*COCl was obtained. The whole quantity was added to the residue of CH_3CH_2*COONa, resulting from evaporation of water from the other half of (I). After 24 h at room temperature, the mixture was heated *in vacuo* from 25° to 100°C over a period of $3-4$ h under collection of a distillate of 9.6 mmole of $(CH_3CH_2$*CO$)_2$O (II). The pyrolysis of (II) was performed as already described.[1] Yield 400 mg or 7 mmole (70 % with respect to CO_2). The infrared gas-spectrum,[2] the PMR-spectrum,[2] and the microwave spectrum [2] showed that the product was pure. Kept at $-190°C$ as crystals, it is stable over a period of at least one year. It contains 55 % methyl-[1-^{13}C] ketene mixed with 45 % ordinary methyl ketene.

A mixture of methyl-[2-^{13}C] ketene and [^{13}C]-methyl ketene. Proceeding as in the previous case, but replacing ethyl bromide by 4.60 g methyl iodide (all other quantities being equal) we prepared an aqueous solution containing 19.9 mmole CH_3*COONa. After complete evaporation of water, 15 ml phthaloylchloride was added. Under a slight vacuum ($650-680$ mm Hg), the mixture was refluxed for 30 min at *ca.* 150°C. CH_3*COCl with a trace of HCl was separated by distillation *in vacuo*. After several single-plate distillations on the vacuum line, during which small quantities of HCl were discarded, 1.534 g or 19.4 mmole CH_3*COCl was obtained. The whole quantity was distilled into a 1.14 m LiAlH$_4$-solution in diethyleneglycol diethylether. After stirring for 1 h, the mixture was cooled (liquid N_2) and 15 ml diethyleneglycol monobutylether added. After the evolution of H_2 had stopped, the flask was heated to room temperature, and the vapors of the reaction mixture removed *in vacuo* over a period of 2 h and condensed in a trap, cooled in liquid N_2. By repeated distillations on the vacuum line, 0.907 g or 19.1 mmole CH_3*CH_2OH was obtained, contaminated only by insignificant