tory dimethylsuccinic acid with m.p. 130—131°. ($[\alpha]_D^{25} = -8°$ in water; anhydride: m.p. 105—107°; $[\alpha]_D^{25} = -117°$ in benzene).

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Infrared Spectra of Some Iodine Cyanide Charge Transfer Complexes

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In a previous paper [1] the infrared spectra of some sulphoxide-iodine cyanide complexes were reported as observed in the sodium chloride region. The donor-acceptor interaction between these molecules was demonstrated by the perturbations of the sulphoxide spectra upon complex formation. Thus, common to all the sulphoxides the S=O stretching mode was shifted to lower wave numbers on co-ordination with iodine cyanide as well as with iodine and iodine monochloride. Therefore, the complex bond is undoubtedly formed from the oxygen atom in the sulphoxides. It is well known [2-4] that also the acceptor spectrum is perturbed on complex formation and for small molecules like iodine cyanide these changes can more easily be interpreted in terms of increasing complex bond strength.

In the present communication we report the spectral behaviour in the C—I stretching region of iodine cyanide when complexes are formed with a group of five different sulphoxides and with diphenyl selenium oxide. Since tetramethylene sulphoxide was not included in the earlier study [1] this molecule was also investigated in the S=O stretching region and the 1:1 formation constant to iodine cyanide determined.

Experimental. The samples of the sulphoxides [1,5,6] and the diphenyl selenium oxide [7] had all been used in the earlier studies. Iodine cyanide from Fluka AG was recrystallized from chloroform. Carbon disulphide and benzene, both *Uvasole* from Merck, were used as solvents. A Perkin-Elmer model 21 spectrometer with sodium chloride optics was employed for the S=O stretching region. The C—I stretching bands were recorded with the aid of a Perkin-Elmer model 337 grating spectrometer. Matched pairs of sealed cells, having the thickness 0.053 and 0.1 cm were used in the two regions, respectively.

The S=O stretching region. When dissolved in carbon disulphide, tetramethylene sulphoxide displays a strong band at 1036 cm^{-1} and a medium intense band at 1093 cm^{-1}. The former is assigned as the S=O stretching mode, the latter as a ring skeleton frequency. When iodine cyanide was added, the 1036 cm^{-1} band decreased in intensity and a new peak assigned as the S=O stretching band of the complex appeared at 1010 cm^{-1}. Thus, the shift on complex formation to iodine cyanide was 26 cm^{-1} compared to 39 cm^{-1} on complex formation to iodine.[6] Using the same method as described earlier, the formation constant for the tetramethylene sulphoxide-iodine cyanide complex was calculated to 91 l/mole at 27 ± 1°C, obtained as an average from three mixed donor-acceptor solutions. The formation constant indicates that tetramethylene sulphoxide forms slightly stronger complexes to iodine cyanide [1] than does dimethyl sulphoxide. The same order of basicity was ob-

tained for the corresponding complexes with iodine by ultraviolet spectroscopical methods.[5,6]

It should be noted that the shifts of the S=O stretching mode on complex formation to iodine cyanide, iodine, the interhalogens, or phenol [8] are considerably lower for tetramethylene than for dimethyl or diethyl sulphoxide. As discussed by Cairns et al.[9] the aliphatic as well as the aromatic sulphoxides exhibit considerable vibrational coupling in the 1060 cm^{-1} region and the "true" position of the S=O stretching frequency can only be roughly estimated. The 1036 cm^{-1} band in tetramethylene sulphoxide is undoubtedly in Fermi resonance with the 1093 cm^{-1} band, but the 1072 and 1069 cm^{-1} bands in dimethyl and diethyl sulphoxide, respectively, are coupled with bands of lower frequencies.[1,9] Therefore, the "true shifts" should be larger for tetramethylene sulphoxide and smaller for dimethyl and diethyl sulphoxide, thus making them of approximately equal magnitude.

The C—I stretching region. Iodine cyanide has three fundamental frequencies and the mode mainly connected with the C—I stretching vibration is situated around 480 cm^{-1} in unpolar solvents. Since carbon disulphide has a very intense absorption band around 400 cm^{-1} and carbon tetrachloride dissolves very small amounts of iodine cyanide, benzene was chosen as the solvent for this study. The weak complex formation between benzene and iodine cyanide will supposedly not interfere significantly with the much stronger sulphoxide complexes.

When any of the present donors were added to a solution of iodine cyanide in benzene, the 476 cm^{-1} band of iodine cyanide was shifted to longer wave lengths. The observed bands are listed in Table 1 and they are assigned as the C—I stretching bands of the complexes. Since the sulphoxides with aromatic substituents have medium intense absorption bands in this region, the complex bands were obtained by inserting a calculated concentration of donor in the reference cell. It appears that the shifts Δv varied between 19 cm^{-1} for the diphenyl and 24 cm^{-1} for the tetramethylene sulphoxide complexes, respectively. The corresponding diphenyl selenium oxide which is a stronger base than the sulphoxides showed a shift of 34 cm^{-1}. No quantitative measurements of the integrated absorption intensities were attempted because of the interfering

Table 1. The C—I stretching band of iodine cyanide on complex formation and the obtained formation constants.

Donor	v [a] cm^{-1}	Δv [a] cm^{-1}	K [b] cm^{-1}
$(C_6H_5)_2SeO$	442	34	—
$(CH_2)_4SO$	452	24	91 [c]
$(C_2H_5)_2SO$	453	23	157
$(CH_3)_2SO$	454	22	86
$(C_6H_5CH_2)_2SO$	455	21	61
$CH_3(C_6H_5)SO$	456	20	35
$(C_6H_5)_2SO$	457	19	32

[a] Solvent: benzene.
[b] Ref. 1, (temperature $27 \pm 1°C$).
[c] This work.

donor bands. However, a monotonic relationship between the shifts and the intensities of the complex band was apparent.

In Fig. 1 the logarithms of the 1:1 formation constants (log K) were plotted against the frequency shifts (Δv) for the various sulphoxide-iodine cyanide complexes. The points (except for tetramethylene sulphoxide) were fitted with a straight line, using the least squares method, and it appears that a reasonable linear relationship was obtained. Tetramethylene sulphoxide which falls outside the plot has a more rigid structure than the other sulphoxides studied because of the lack of internal rotational freedom. Thus, the change in entropy on complex formation might be somewhat different for this molecule, resulting in a smaller formation
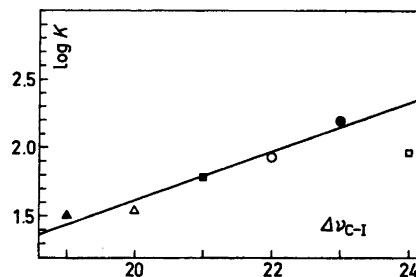

Fig. 1. Plot of log K *versus* the frequency shifts (Δv). O dimethyl, ● diethyl, ☐ tetramethylene, ■ dibenzyl, △ methyl phenyl and ▲ diphenyl sulphoxide.

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

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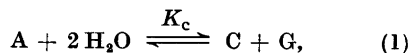
where $K_c = [C][G]/[A][H_2O]^2$

(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)
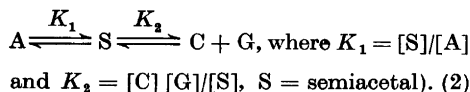
Let us denote

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

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