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Molecular Complexes of Organic Carbonates with Lewis Acids

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Some compounds of Ti^{IV}, Al^{III}, Sn^{IV} have been employed as catalysts in the synthesis of aromatic carbonates from alkyl carbonates [1]. We suggest that the catalytic activity may be explained in terms of complexes that dimethylcarbonate (DMC) forms with some Lewis acids (*e.g.* $TiCl_4$, $AlCl_3$).

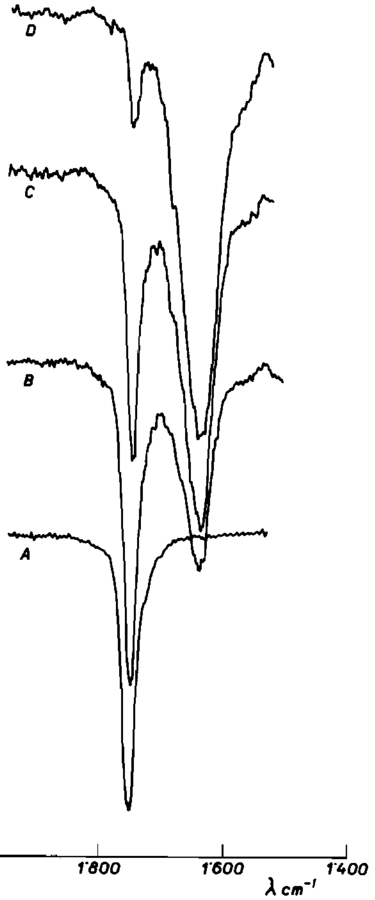

Fig. 1. Changes of the C–O stretching of DMC with $TiCl_4$ concentration (DMC concentration is 35.6 mmol/l). Curve A = DMC; Curve B, C, D: $TiCl_4$/DMC = 0.30, 0.75, 2.5.

The IR spectra reported in Fig. 1, relative to the carbonylic band of the DMC and of the interaction compound of DMC with $TiCl_4$, recorded with various molar ratios $TiCl_4$/DMC (R), show in CH_2Cl_2 a sensible shift of the C–O stretching from 1750 cm^{-1} to 1640 cm^{-1}, due to the diminished double-bond character of the C=O bond. The CH_3O–C stretching band shows a shift to higher wavenumber (from 1275 to 1350 cm^{-1}) probably due to a greater double-bond character of the CH_3O–C bond in the complex.

In order to obtain some quantitative data about the stability of these complexes as a function of carbonate basicity and Lewis acid strength we have recorded NMR spectra in CH_2Cl_2 of the following systems: $TiCl_4$–DMC, Diethylcarbonate (DEC), Ethylphenylcarbonate (EFC) and $AlEtCl_2$, $SnCl_4$–DMC. The stability constants of these compounds were calculated by the Benesi–Hildebrand method [2] as applied to NMR spectrometry by Hanna *et al.* [3].

In accordance with the Gutowsky–Saike theory [4] the chemical shifts of the hydrogen atoms of the carbonate, in a fast exchange between the non-complexed (D) and complexed (AD) states, follow the relationship:

$$\delta = x\delta_0^D + x_c\delta_c^D \qquad (1)$$

where δ_0^D and δ_c^D are chemical shifts, relative to an arbitrary reference, of non complexed and complexed D, x and x_c are respectively the molar fractions of non complexed and complexed D.

If we take the solvent as reference and assume

$$\Delta_0 = \delta_0^D - \delta_c^D \text{ and } \Delta_{obs} = \delta_0^D - \delta$$

when $|A_0| \gg |D_0|$ we obtain

$$\frac{1}{\Delta_{obs}} = \frac{1}{K\Delta_0}\,\frac{1}{|A_0|} + \frac{1}{\Delta_0} \qquad (2)$$

where $|A_0|$ and $|D_0|$ are the initial concentrations of the acceptor and donor and K is the formation constant of the AD complex. If we plot $1/\Delta_{obs}$ *versus* $1/|A_0|$ it is possible to obtain the value of K (Fig. 2, 3). These plots are obtained using a fixed concentration of the carbonate (10^{-2} *M*) and varying the concentration of the Lewis acid (10^{-1} + 1 *M*).

In Table I we report the formation constants at 25 °C and the values of the parameters calculated in accordance with [2]. The formation constants of the complexes follow the same order of carbonate basicity:

DEC > DMC > EFC

With reference to the Lewis acids employed, we note that the plot for the system DMC–$AlEtCl_2$ is not linear, due probably to the association of the aluminum compound.

The sequence observed is

$TiCl_4 > AlEtCl_2 > SnCl_4$

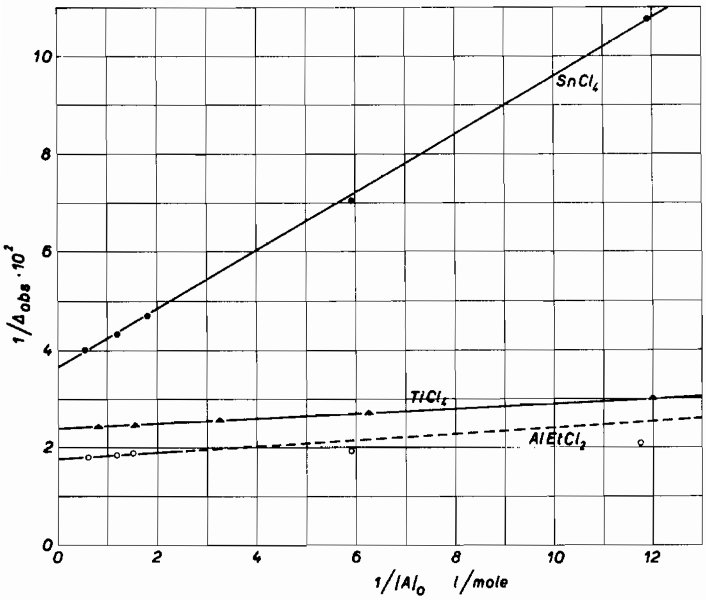

Fig. 2. Plot of $1/\Delta_{obs}$ *versus* $1/A_0$ for the complexes of DMC with different Lewis acids.

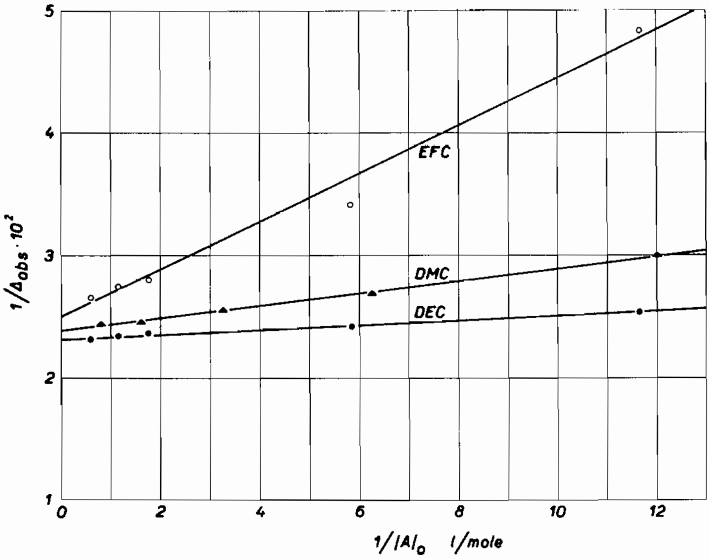

Fig. 3. Plot of $1/\Delta_{obs}$ *versus* $1/A_0$ for the complexes of $TiCl_4$ with different organic carbonates.

TABLE I. Parameters of Equation (2) Calculated for Various Complexes.

System	Intercept	Slope	K (l/mol)
DMC + $TiCl_4$	2.385	4.99	4.78 X 10
DMC + $SnCl_4$	3.665	56.83	6.45
DMC + $AlEtCl_2$	1.731	10.88	1.59 X 10
DEC + $TiCl_4$[a]	2.317	1.85	1.24 X 10^2
EFC + $TiCl_4$[a]	2.568	14.42	1.78 X 10

[a]Calculated on the ethyl quartet center.

TABLE II. Chemical Shifts of DMC in the Complexes with Different Lewis Acids.

Compound	τ
DMC	6.29
DMC + $SnCl_4$	6.02[a]
DMC + $TiCl_4$	5.87[a]
DMC + $AlEtCl_2$	5.71[a]

[a]τ values extrapolated.

but the shift values found (Table II) show that $AlEtCl_2$ is a more powerful acceptor than $TiCl_4$ and $SnCl_4$, *etc.*

The shifts in the carbonylic bands of IR spectra and the high values of formation constants of these complexes suggest that between organic carbonates and Lewis acids there exists a strong n → v bond rather than a CT type bond, as reported for complexes of carbonates with SO_2 [5].

References

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