Kinetic Studies of Lewis Acidity. Part I. Anionotropic Rearrangement of 1-Phenylprop-2-en-1-ol catalysed by Aluminium(III), Antimony(III), Antimony(V), Boron(III), Gallium(III), Phosphorus(III), Phosphorus(V), Phosphoryl, Tin(IV), Titanium(IV), and Zinc(II) Chlorides

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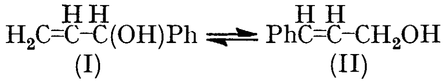
In sulpholan solution 1-phenylprop-2-en-1-ol undergoes an anionotropic rearrangement to cinnamyl alcohol in the presence of metal and non-metal chloride Lewis acids. The rates of rearrangement are first order with respect to the alcohol. and are directly proportional to the concentration of the catalyst. A general mechanism is proposed. Relative rate constants for the rearrangement at 35° are: $GaCl_3$ 350. $SnCl_4$ 74. PCl_5 38. $SbCl_5$ 26. $POCl_3$ 21. $TiCl_4$ 9·3. $AlCl_3$ 6·5. BCl_3 3·9. PCl_3 2·8. HCl 1·0. $SbCl_3$ $4{\cdot}1 \times 10^{-2}$. and $ZnCl_2$ $9{\cdot}1 \times 10^{-6}$.

Most quantitative studies of Lewis acidity have involved measurements of equilibrium constants, using i.r. or n.m.r. techniques, of complex formation between the acid (electron-pair acceptor) and a variety of bases (donors).[1] Kinetic comparisons of Lewis acids have included studies of the depolymerisation of paraldehyde,[2] the decomposition of benzazide,[3] the Friedel–Crafts benzoylation of toluene and chlorobenzene,[4] the disproportionation of ethyltrimethylsilane,[5] the deuteriation of benzene with deuterium bromide,[6] and the racemisation of optically active α-methylbenzyl chloride.[7,8] No attempt was made until recently[8,9] to compare the catalytic reactivities in terms of the mechanism of the reactions.



$$\mathrm{H_2C{=}\overset{H}{C}{-}\overset{H}{C}(OH)Ph \rightleftharpoons Ph\overset{H}{C}{=}\overset{H}{C}{-}CH_2OH}$$

(I) (II)

The present contribution describes our study of the kinetics of the anionotropic rearrangement of 1-phenylprop-2-en-1-ol (I) to 3-phenylprop-2-en-1-ol (cinnamyl alcohol) (II) under the catalytic influence of several metal and non-metal chlorides. The same molecular rearrangement [(I) $\rightleftharpoons$ (II)] has been studied for mineral acids in aqueous ethanolic or aqueous dioxan solutions,[10] and for the Lewis acid boron(III) fluoride in anhydrous dioxan solution.[11] In each case formation of the conjugated isomer (II) was nearly quantitative (*ca.* 95%). Other, but unrelated, instances of anionotropic rearrangements catalysed by Lewis acids are also known.[12]

The anionotropic rearrangement [(I) $\rightleftharpoons$ (II)] has now been found to proceed in the presence of many

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Lewis acids. In anhydrous sulpholan solution these rearrangements were mostly very rapid. The kinetics could be measured spectrophotometrically for dilute solutions, both in respect of the 1-phenyl isomer (I) (usually $1{\cdot}5 \times 10^{-4}$M) and of the catalyst (normally *ca.* 10^{-5}—10^{-4}M), by following the appearance of the conjugation chromophore of cinnamyl alcohol (II) at 284 nm. Comparison of the u.v. light absorption of the

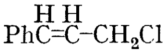
Rate constants, and derived data, for the rearrangement of 1-phenylprop-2-en-1-ol ($1{\cdot}5 \times 10^{-4}$M) in sulpholan solution, catalysed by metal and non-metal chlorides

Catalyst		Rate constants k_1/min^{-1} (°C) [a]	$k_1^{35°}$/s^{-1} (computed)	Normalised rate constant $k_n^{35°}$ l mol^{-1} s^{-1} [b]	E_a/kcal mol^{-1} [c]	log A	$\Delta S^‡$ (35°)/cal mol^{-1} K^{-1}	$\Delta G^‡$ (35°)/kcal mol^{-1}
Formula	Concentration (M)							
$GaCl_3$	$1{\cdot}0 \times 10^{-5}$	$0{\cdot}54 \pm 0{\cdot}01$ (34·4)	$9{\cdot}00 \times 10^{-3}$	900				
	$1{\cdot}70 \times 10^{-5}$	$0{\cdot}98 \pm 0{\cdot}07$ (34·4)						
	$2{\cdot}40 \times 10^{-5}$	$1{\cdot}32 \pm 0{\cdot}04$ (34·4)						
	$3{\cdot}10 \times 10^{-5}$	$1{\cdot}72 \pm 0{\cdot}09$ (34·4)						
	$3{\cdot}80 \times 10^{-5}$	$2{\cdot}35 \pm 0{\cdot}33$ (34·4)						
$SnCl_4$	$3{\cdot}80 \times 10^{-5}$	$0{\cdot}59 \pm 0{\cdot}03$ (35·0)						
	$7{\cdot}50 \times 10^{-5}$	$1{\cdot}05 \pm 0{\cdot}01$ (35·0)						
	$1{\cdot}00 \times 10^{-4}$	$0{\cdot}78 \pm 0{\cdot}05$ (29·1),	$2{\cdot}10 \times 10^{-2}$	209	14·5	12·63	−2·8	14·8
		$1{\cdot}24 \pm 0{\cdot}03$ (34·5),						
		$1{\cdot}64 \pm 0{\cdot}02$ (38·6),						
		$1{\cdot}97 \pm 0{\cdot}24$ (41·3),						
		$2{\cdot}83 \pm 0{\cdot}10$ (45·8)						
	$1{\cdot}41 \times 10^{-4}$	$1{\cdot}85 \pm 0{\cdot}09$ (35·0)						
	$2{\cdot}42 \times 10^{-4}$	$3{\cdot}26 \pm 0{\cdot}34$ (35·0)						
	$2{\cdot}82 \times 10^{-4}$	$3{\cdot}71 \pm 0{\cdot}03$ (35·0)						
PCl_5	$9{\cdot}70 \times 10^{-5}$	$0{\cdot}57 \pm 0{\cdot}05$ (35·2)						
	$2{\cdot}00 \times 10^{-4}$	$1{\cdot}33 \pm 0{\cdot}07$ (35·2)	$2{\cdot}16 \times 10^{-1}$	108				
	$2{\cdot}57 \times 10^{-4}$	$1{\cdot}79 \pm 0{\cdot}05$ (35·2)						
$SbCl_5$	$4{\cdot}5 \times 10^{-5}$	$0{\cdot}20 \pm 0{\cdot}015$ (34·2)	$3{\cdot}33 \times 10^{-3}$	74				
$POCl_3$	$5{\cdot}30 \times 10^{-5}$	$0{\cdot}21 \pm 0{\cdot}01$ (36·1),	$3{\cdot}24 \times 10^{-3}$	60·3	11·6	10·04	−14·7	15·6
		$0{\cdot}32 \pm 0{\cdot}02$ (44·0),						
		$0{\cdot}44 \pm 0{\cdot}03$ (49·3),						
		$0{\cdot}64 \pm 0{\cdot}03$ (55·7),						
		$0{\cdot}85 \pm 0{\cdot}04$ (61·0)						
	$6{\cdot}60 \times 10^{-5}$	$0{\cdot}26 \pm 0{\cdot}02$ (36·6)						
	$9{\cdot}80 \times 10^{-5}$	$0{\cdot}41 \pm 0{\cdot}02$ (36·6)						
	$1{\cdot}40 \times 10^{-4}$	$0{\cdot}53 \pm 0{\cdot}02$ (36·6)						
	$2{\cdot}00 \times 10^{-4}$	$0{\cdot}80 \pm 0{\cdot}02$ (36·6)						
	$2{\cdot}57 \times 10^{-4}$	$1{\cdot}03 \pm 0{\cdot}02$ (36·6)						
	$3{\cdot}30 \times 10^{-4}$	$1{\cdot}28 \pm 0{\cdot}00$ (36·6)						
$TiCl_4$	$4{\cdot}60 \times 10^{-5}$	$0{\cdot}09 \pm 0{\cdot}01$ (35·3)						
	$9{\cdot}20 \times 10^{-5}$	$0{\cdot}16 \pm 0{\cdot}01$ (35·3)						
	$1{\cdot}44 \times 10^{-4}$	$0{\cdot}25 \pm 0{\cdot}01$ (35·3)						
	$1{\cdot}80 \times 10^{-4}$	$0{\cdot}28 \pm 0{\cdot}00$ (35·3),	$4{\cdot}75 \times 10^{-3}$	26·2	14·0	11·32	−8·8	16·1
		$0{\cdot}51 \pm 0{\cdot}04$ (42·5),						
		$0{\cdot}70 \pm 0{\cdot}03$ (47·7),						
		$0{\cdot}95 \pm 0{\cdot}04$ (52·3),						
		$1{\cdot}32 \pm 0{\cdot}04$ (57·6)						
	$2{\cdot}32 \times 10^{-4}$	$0{\cdot}39 \pm 0{\cdot}01$ (35·3)						
$AlCl_3$	$1{\cdot}50 \times 10^{-4}$	$0{\cdot}21 \pm 0{\cdot}01$ (36·9),	$2{\cdot}78 \times 10^{-3}$	18·9	17·9	13·97	+3·3	16·3
		$0{\cdot}36 \pm 0{\cdot}02$ (43·1),						
		$0{\cdot}55 \pm 0{\cdot}02$ (49·0),						
		$1{\cdot}09 \pm 0{\cdot}05$ (55·3),						
		$1{\cdot}64 \pm 0{\cdot}06$ (60·8)						
	$3{\cdot}30 \times 10^{-4}$	$0{\cdot}43 \pm 0{\cdot}02$ (36·9)						
	$4{\cdot}80 \times 10^{-4}$	$0{\cdot}71 \pm 0{\cdot}03$ (36·9)						
	$6{\cdot}20 \times 10^{-4}$	$0{\cdot}83 \pm 0{\cdot}00$ (36·9)						
	$7{\cdot}80 \times 10^{-4}$	$1{\cdot}01 \pm 0{\cdot}04$ (36·9)						
BCl_3	$2{\cdot}10 \times 10^{-4}$	$0{\cdot}14 \pm 0{\cdot}005$ (34·9)	$2{\cdot}35 \times 10^{-3}$	11·2	8·83	7·31	−27·2	16·6
		$0{\cdot}19 \pm 0{\cdot}01$ (41·0),						
		$0{\cdot}24 \pm 0{\cdot}00$ (47·4),						
		$0{\cdot}33 \pm 0{\cdot}02$ (54·5),						
		$0{\cdot}47 \pm 0{\cdot}04$ (62·8)						
	$3{\cdot}10 \times 10^{-4}$	$0{\cdot}20 \pm 0{\cdot}01$ (35·6)						
	$4{\cdot}50 \times 10^{-4}$	$0{\cdot}28 \pm 0{\cdot}01$ (35·6)						
	$7{\cdot}30 \times 10^{-4}$	$0{\cdot}49 \pm 0{\cdot}01$ (35·6)						
	$1{\cdot}05 \times 10^{-3}$	$0{\cdot}67 \pm 0{\cdot}02$ (35·6)						
	$1{\cdot}45 \times 10^{-3}$	$0{\cdot}91 \pm 0{\cdot}00$ (35·6)						
PCl_3	$5{\cdot}20 \times 10^{-4}$	$0{\cdot}25 \pm 0{\cdot}00$ (36·7),	$4{\cdot}12 \times 10^{-3}$	7·82	6·19	5·28	−36	16·8
		$0{\cdot}32 \pm 0{\cdot}03$ (42·3),						
		$0{\cdot}36 \pm 0{\cdot}01$ (47·1),						
		$0{\cdot}42 \pm 0{\cdot}01$ (52·6),						
		$0{\cdot}50 \pm 0{\cdot}02$ (59·0)						
	$5{\cdot}50 \times 10^{-4}$	$0{\cdot}24 \pm 0{\cdot}01$ (36·7)						
	$1{\cdot}40 \times 10^{-3}$	$0{\cdot}76 \pm 0{\cdot}04$ (36·7)						
	$1{\cdot}80 \times 10^{-3}$	$0{\cdot}88 \pm 0{\cdot}01$ (36·7)						
	$2{\cdot}85 \times 10^{-3}$	$1{\cdot}44 \pm 0{\cdot}08$ (36·7)						

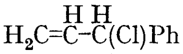
Catalyst Formula	Catalyst Concentration (M)	Rate constants k_1/ min^{-1} (°C) [a]	$k_1^{35°}/s^{-1}$ (computed)	Normalised rate constant $k_n^{35°}$ $l\ mol^{-1}\ s^{-1}$ [b]	E_a/kcal mol^{-1} [c]	log A	$\Delta S^‡$ (35°)/ cal mol^{-1} K^{-1}	$\Delta G^‡$ (35°)/ kcal mol^{-1}
HCl(aq)	2·00 × 10^{-3}	0·31 ± 0·02 (33·5), 0·36 ± 0·02 (37·2), 0·44 ± 0·04 (45·3), 0·55 ± 0·04 (52·1), 0·62 ± 0·03 (59·4)	5·70 × 10^{-3}	2·76	5·46	4·31	−41	17·4
	2·80 × 10^{-3}	0·54 ± 0·08 (36·5)						
	3·80 × 10^{-3}	0·69 ± 0·04 (36·5)						
	4·90 × 10^{-3}	0·91 ± 0·03 (36·5)						
	5·60 × 10^{-3}	1·02 ± 0·05 (36·5)						
$SbCl_3$ [d]	1·40 × 10^{-3}	0·10 ± 0·00 (64·4)						
	2·80 × 10^{-3}	0·21 ± 0·00 (64·4)						
	4·60 × 10^{-3}	0·29 ± 0·01 (64·4)						
	5·60 × 10^{-3}	0·14 ± 0·02 (51·8), 0·23 ± 0·00 (58·0), 0·30 ± 0·01 (62·5), 0·39 ± 0·02 (66·0), 0·56 ± 0·02 (71·8)	6·55 × 10^{-4}	0·116	15·4	9·95	−15·0	19·4
	6·00 × 10^{-3}	0·36 ± 0·01 (64·4)						
	7·30 × 10^{-3}	0·46 ± 0·02 (64·4)						
$ZnCl_2$	9·0 × 10^{-2}	1·4 × 10^{-4} (36·6)	(2·3 × 10^{-6})	2·6 × 10^{-5}				

[a] Mean values of at least four kinetic runs. [b] Computed k_1 (at 35°)/concentration of catalyst. [c] $\Delta H^‡$ Values are lower by *ca.* 610 cal mol^{-1}. [d] Concentration of alcohol (I) was 3·0 × 10^{-4}M.

solution of the rearranged product with that of pure *trans*-cinnamyl alcohol (II) showed that in general >90% of the latter was formed under the conditions of the kinetic runs. The u.v. light absorption of the product of rearrangement gradually increases in the region of the low-intensity absorption band near 280—305 nm, owing possibly to *trans–cis* isomerisation of alcohol


$PhC(H){=}C(H){-}CH_2Cl$

(III)


$H_2C{=}C(H){-}C(H)(Cl)Ph$

(IV)

(II), but more probably mainly to the slow conversion of alcohol (II) into cinnamyl chloride (III). The formation of cinnamyl chloride (III) from the 1-phenyl isomer (I) was reported [13] to occur on treatment with phosphorus(III), phosphorus(V), or thionyl chloride in ether solution, in the presence or in the absence of added pyridine or diethylamine. Allyl chlorides are believed to be capable of undergoing acid-catalysed isomeric rearrangements.[14] Isomerisation of 1-chloro-1-phenylprop-2-ene (IV) to cinnamyl chloride (III) appeared to take place under the influence of traces of hydrogen chloride.[13] It is therefore possible that in addition to the normal mode of formation in our systems of cinnamyl chloride (III), *i.e. via* the route (I) ⟶ (II) ⟶ (III), a small amount can also be formed *via* the route (I) ⟶ (IV) ⟶ (III). Rearrangements carried out at higher concentrations of alcohol (I) and the catalyst (*e.g.* $SnCl_4$, $AlCl_3$, or PCl_5) showed the formation of cinnamyl alcohol (II) and up to 9% yield of cinnamyl chloride (III), as well as products of higher molecular weight.

Reproducible rate coefficients for the rearrangements could be obtained by the use of an iterative Newton–Raphson procedure, programmed for the Elliott 803 digital computer. A similar method for the analysis of second-order rate data has been used previously.[15] The rate constants were first-order with respect to the alcohol (I), and were directly proportional to the concentrations of each catalyst. The kinetic results obtained at the most appropriate catalyst concentrations for a range of temperatures, together with the derived thermodynamic parameters, are summarised in the Table.

For the powerful catalysts $GaCl_3$, PCl_5, and $SbCl_5$ reliable rate constants could be obtained only at low temperatures. It was not feasible to effect an improvement either by lowering the concentration of alcohol, since the solution would then have become too transparent in the usable region of the spectrum, or by lowering the concentration of the catalyst (*ca.* 10^{-5}M). In spite of very careful work under dry nitrogen 'ageing effects' were observed with the catalyst solutions, *i.e.* a progressive lowering of the observed rates of rearrangement with time, due probably to adsorption of the catalyst on the glass surfaces and of catalyst deactivation by trace amounts of water. At the other extreme zinc(II) chloride proved to be only very weakly catalytic for the anionotropic rearrangement of the alcohol (I); its rate of rearrangement was obtained only approximately, when needed in connection with other work.[16]

Attempts were made to obtain kinetic data for two other well-known Lewis acids, zirconium(IV) and iron(III) chlorides. Zirconium(IV) chloride dissolved only very slightly in the solvent sulpholan, and its saturated solution was not catalytically active. Iron(III) chloride readily dissolved in the solvent to give a highly coloured solution, which even at low concentrations absorbed light too strongly in the appropriate region of the u.v. spectrum.

For a comparison to be made between our Lewis acids and a mineral acid, the anionotropy of the alcohol (I)

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was also studied in the presence of hydrochloric acid in sulpholan solution. This acid was introduced in the form of 10N-hydrochloric acid, which thereby introduced 0·0088—0·0246M-water into the medium; it is probable that this has only a very small effect on the reaction rates measured. The catalytic activities of $GaCl_3$, $SnCl_4$, PCl_5, $SbCl_5$, $POCl_3$, $TiCl_4$, $AlCl_3$, BCl_3, and PCl_3 are all greater than that of HCl(aq). $SbCl_3$ and $ZnCl_2$ are appreciably weaker catalysts than the mineral acid.

It is inevitable that, in spite of stringent precautions, small traces of water will be present in the reaction media. One must therefore consider what influence water might have in the kinetic system. With water certain Lewis acids (*e.g.* $AlCl_3$) give hydrates, which can act as Friedel–Crafts catalysts,[17] though with reduced activity.[18] The catalysis is of the Brønsted type,[18] due to ionisation of the hydrate, *e.g.* $AlCl_3,OH_2 \rightleftharpoons HOAlCl_3^- + H^+$. A small amount of water in the system must compete, in terms of complex formation, with a high concentration of solvent molecules ([sulpholan] = 12·4M). It is unlikely, therefore, that the catalytic activity of a Lewis acid in our system is due solely to that of its hydrate. Instead, a small amount of the hydrate will modify (*i.e.* generally reduce) slightly the catalytic powers of the Lewis acid. Analogously, it has been shown that boron(III) fluoride monohydrate, BF_3,OH_2, catalyses the rearrangement of the alcohol (I) (k_1 at 25° = $8{\cdot}0 \times 10^{-3}$ min^{-1}) at about one-third the rate of anhydrous boron(III) fluoride (k_1 at 25° = $2{\cdot}3 \times 10^{-2}$ min^{-1}).[11] It cannot be decided upon the evidence presented here whether the catalysts are the acid–sulpholan adducts, or the acid–water adducts. A detailed study of the rate-decreasing effect of added water on the catalysis by tin(IV) chloride will be presented in a later paper.[19]

The relative catalytic efficiencies of the non-metal chlorides, as gauged from the normalised rate constants at 35° (Table), were found to be $PCl_5 > POCl_3 > BCl_3 > PCl_3 > HCl$. The reactivities span only *ca.* 1·5 orders of magnitude; this closeness of catalytic activity is reflected in the fairly narrow range of the free energies of activation ($\Delta G^\ddagger$ = 15·6—17·4 kcal mol^{-1}). The reactivities of the metal chloride catalysts, however, cover comparatively a much wider range, spanning 7·5 orders of magnitude, and this is seen also in a wider range of $\Delta G^\ddagger$ values (14·8—19·4 kcal mol^{-1}).

The activation energies for the metal chloride catalysts, which range from 17·9 ($AlCl_3$) to 14·0 kcal mol^{-1} ($TiCl_4$), are all much higher than for the non-metal chloride catalysts of the present series (5·5—11·6 kcal mol^{-1}). Again, the entropies of activation ($\Delta S^\ddagger$) for the non-metal chlorides were found in the range —15 to —41 cal mol^{-1} K^{-1}, whereas those for the metal chlorides were much higher, *viz.* +2·8 to —15 cal mol^{-1} K^{-1}. Whereas the thermodynamic parameters ($\Delta H^\ddagger$, $\Delta S^\ddagger$) for the metallic and the non-metallic chlorides seem to be clearly differentiated, the actual rate constants are not. A plot of $\Delta H^\ddagger$ *vs.* $\Delta S^\ddagger$ for the anionotropy of the alcohol (I) with seven of the eight catalysts for which data are available is satisfactorily rectilinear (correlation coefficient 0·992). The slope of this line is 269·7 K, rather below the mean experimental temperature. A measure of compensation therefore exists between $\Delta H^\ddagger$ and $\Delta S^\ddagger$, except for the catalyst $SbCl_3$, so as to keep the free energy of activation, $\Delta G^\ddagger$, within a reasonably narrow range (*cf.* the 'Compensation Law'[20]).

The overall order of catalytic efficiencies for our rearrangement can be given as: $GaCl_3 > SnCl_4 > PCl_5 > SbCl_5 > POCl_3 > TiCl_4 > AlCl_3 > BCl_3 > PCl_3 >$ HCl(aq) $> SbCl_3 > ZnCl_2$. Against this sequence we have a general sequence of Lewis acidity, predicted from various data:[2,21] $BCl_3 > AlCl_3 > GaCl_3 > SbCl_5 > SnCl_4 > ZnCl_2$. In agreement with our results there is some evidence in the literature that, as Lewis acids, $SnCl_4 > PCl_5$,[22] $BCl_3 > PCl_3$,[23] and $GaCl_3 > AlCl_3 > BCl_3$.[24] In contrast with our findings, however, are the observed sequences of acidities: $AlCl_3 > PCl_5$,[25] $AlCl_3 > POCl_3$,[26] $BCl_3 > POCl_3$,[27] $SbCl_5 > PCl_5$.[21] These results suggest that catalytic efficiency in our system is mechanistically related to, but not exactly the same as, the measure of precise Lewis acidity. This is not surprising since (see below) we are comparing not the free halides but their complexes with the solvent sulpholan: a strong Lewis acid may form a stable complex with the solvent, and this complex may then be a weak catalyst for the molecular rearrangement.

Any mechanism for these anionotropic rearrangements (and certainly there will be mechanistic variants for each catalyst system) must account for the following experimental observations: (a) that the rate constant is proportional to the concentration of the catalyst in the medium, and (b) that the rearrangement shows first-order dependence on the alcohol (I). In solution a metal halide will complex with one or more molecules of the relatively weakly basic sulpholan, (S), which is present in large excess ($[S] = 10^6[MCl_x]$). Therefore, equilibrium (i) (see Scheme) must lie well over to the right. The concentration of the catalyst MCl_x,S_y will determine the concentration of the alcohol species [(VIa or b)] available for rearrangement. Step (iia) [or alternatively (iib)] results when the alcohol (I) is

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added to the catalyst solution. In no case was a gradual build-up of the rate of rearrangement observed. Therefore, equilibrium (ii) is rapidly attained in practice.

$$\mathrm{MCl}_x + y\mathrm{S} \rightleftharpoons \mathrm{MCl}_x,S_y\ (\mathrm{V}) \qquad \text{(i)}$$

$$\underset{\mathrm{A}}{\mathrm{MCl}_x,S_y} + \underset{\mathrm{B}}{\mathrm{ROH}} \overset{K_1}{\rightleftharpoons} \underset{\mathrm{C}}{\mathrm{MCl}_x,\mathrm{ROH}}\ (\mathrm{VIa}) + y\mathrm{S} \qquad \text{(iia)}$$

$$\text{or }\ \mathrm{MCl}_x,S_y + \mathrm{ROH} \rightleftharpoons \mathrm{MCl}_x,\mathrm{ROH},\ S_{y-1}\ (\mathrm{VIb}) + \mathrm{S} \qquad \text{(iib)}$$

$$\underset{\mathrm{C}}{\mathrm{MCl}_x,\mathrm{ROH}} \underset{k_{-r}}{\overset{k_r}{\rightleftharpoons}} \underset{\mathrm{D}}{\mathrm{MCl}_x,\mathrm{R'OH}} \qquad \text{(iii)}$$

$$\underset{\mathrm{D}}{\mathrm{MCl}_x,\mathrm{R'OH}} + y\mathrm{S} \overset{K_2^{-1}}{\rightleftharpoons} \underset{\mathrm{A}}{\mathrm{MCl}_x,S_y} + \underset{\mathrm{E}}{\mathrm{R'OH}} \qquad \text{(iv)}$$

SCHEME R = $\mathrm{H_2C{=}CH{-}CHPh{-}}$, R′ = $\mathrm{PhCH{=}CH{-}CH_2{-}}$

On the assumption that (iii) (see Scheme) is the rate-determining step, *i.e.* that the attainment of equilibria in (ii) and (iv) is rapid compared to the rearrangement step (iii), we may write equations (v) and (vi) where K_1

$$[\mathrm{C}] = K_1[\mathrm{A}][\mathrm{B}] \qquad \text{(v)}$$

$$[\mathrm{D}] = K_2[\mathrm{A}][\mathrm{E}] \qquad \text{(vi)}$$

and K_2 are equilibrium constants for reaction (ii) and (reverse) reaction (iv), respectively. The assumptions are here made that K_1 and K_2 are both small, *i.e.* that both alcohols are present in the medium essentially completely in uncomplexed form. The u.v. light absorption of the solutions seems to bear this out. The rate of formation of D (and therefore of E) is then given by (vii).

$$\begin{aligned}\text{Rate} &= k_r[\mathrm{C}] - k_{-r}[\mathrm{D}]\\ &= k_rK_1[\mathrm{A}][\mathrm{B}] - k_{-r}K_2[\mathrm{A}][\mathrm{E}] \qquad \text{(vii)}\end{aligned}$$

Let the initial concentrations of A and B be a and b, respectively. Let the decrease in concentration of B at time t be x. Then, at time t, [B] = $b - x$, and [E] = x. It follows that the concentration of A remains constant throughout at the initial value a. Equation (vii) then becomes (viii). At equilibrium $\mathrm{d}x/\mathrm{d}t = 0$. Therefore

$$\begin{aligned}-\mathrm{d}x/\mathrm{d}t &= k_rK_1a(b - x) - k_{-r}K_2ax\\ &= k_rK_1ab - (k_rK_1 + k_{-r}K_2)ax \qquad \text{(viii)}\end{aligned}$$

$k_rK_1ab = (k_rK_1 + k_{-r}K_2)ax_e$, where x_e is the equilibrium value of x (*i.e.* the equilibrium concentration of E). Expression (ix) follows. The (second-order) normalised

$$\mathrm{d}x/\mathrm{d}t = (k_rK_1 + k_{-r}K_2)a(x_e - x) \qquad \text{(ix)}$$

rate constant k_n is then given in expression (x) and the observed (pseudo-first-order) rate constant k_1 in expression (xi). Thus $k_n = k_1/a$. The equilibrium ratio of the product alcohol E [(II)] to the reactant alcohol B [(I)] is given in expression (xii). Experimentally, this ratio was found to be *ca.* 20. Thus, $k_rK_1 \gg k_{-r}K_2$, and the observed rate constant can, to a reasonable approximation, be interpreted simply as the rate constant for the overall forward reaction.

$$k_n = (k_rK_1 + k_{-r}K_2) \qquad \text{(x)}$$

$$k_1 = (k_rK_1 + k_{-r}K_2)a \qquad \text{(xi)}$$

$$\frac{[\mathrm{E}]_e}{[\mathrm{B}]_e} = \frac{[\mathrm{D}]_eK_1}{[\mathrm{C}]_eK_2} = \frac{k_rK_1}{k_{-r}K_2} \qquad \text{(xii)}$$

EXPERIMENTAL

An atmosphere of dry nitrogen was maintained over (momentarily) exposed sulpholan (or its solutions) during the mixing operations.

Materials.—Substrate. 1-Phenylprop-2-en-1-ol was obtained [28] as an oil, b.p. 90—91° at 1·8 mmHg, n_D^{20} 1·5448 (lit.,[10a] $n_D^{14\cdot5}$ 1·5464).

Solvents. (a) Sulpholan. The method of purification was similar to that reported by Schofield and his coworkers; [29] other methods [30] were found to be less reliable. Commercial sulpholan (2 kg) was allowed to stand for 3 days over molecular sieve (4A, 200 g; activated by heating at 150° for 12 h), with occasional shaking. To the decanted solvent phosphoric oxide (75 g) was added in portions, and the mixture stirred several times. Portions (500 ml) of the solvent were then again decanted, and distilled *in vacuo*, b.p. 120° at 0·2 mmHg, using a rotary evaporator (Büchi Rotavapor-R). The combined distillates were then stored over molecular sieve in the dark. For the kinetic runs the solvent was again decanted, and redistilled, only the middle fraction being used. Pure sulpholan had m.p. 28·5° (lit.,[31] m.p. 28·45°), n_D^{30} 1·4829 (lit.,[32] n_D^{30} 1·4820), and specific conductance $<2 \times 10^{-8}$ ohm^{-1} cm^{-1}. Sulpholan was transparent above 200 nm, contained $<0{\cdot}7$ mol % of unsaturated (bromine tiration), and $<2 \times 10^{-3}$ g per 100 ml of water (Karl Fischer).[33]

(b) Carbon tetrachloride. AnalaR carbon tetrachloride was shaken with concentrated sulphuric acid, separated, and distilled from phosphoric oxide.

Catalysts. The solid catalysts were initially kept *in vacuo* over phosphoric oxide for several days. They were then purified by repeated sublimation under a reduced nitrogen atmosphere. Initial sublimation of aluminium chloride was carried out after admixture with aluminium powder. Zinc chloride was dried [34] by means of thionyl chloride. Gallium chloride (Koch–Light, '99·99%') was used without further treatment. The liquid catalysts were purified by repeated fractional distillation under dry nitrogen; the b.p.s were: tin(IV) chloride 114°, titanium(IV) chloride 136°, antimony(V) chloride 139°, boron(III) chloride 10°, phosphorus(III) chloride 74°, and phosphoryl chloride 104°.

Catalysts were initially prepared as stock solutions (normally 0·1—0·6M) in pure sulpholan; these stock solutions were diluted with more sulpholan, in two or three stages, to give very dilute catalyst solutions for the kinetic runs.

Kinetic Procedure.—The kinetic runs were conducted in

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1 cm silica absorption cells, maintained at constant temperature in a thermostatted cell-holder and cell-housing, fitted to a (manual) Unicam SP 500 spectrophotometer. Temperatures could be maintained to within ±0·01° at 35°, or ±0·14° at 50°.

Into dry cells at 35° were placed 3·00 ml of working catalyst solutions (by means of a S 43–960 Griffen pipette filler), the air-space replaced by dry nitrogen, stoppers (polytetrafluoroethylene) fitted, and the cells placed in the cell holder to equilibrate. To the solution cell was then added the appropriate volume (*ca.* 0·02 ml) of alcohol stock solution (prepared in the carrier solvent carbon tetrachloride), by means of the fine nozzle of a graduated micrometer syringe (Agla syringe, Burroughs Wellcome and Co.). The nitrogen atmosphere was renewed, the stopper replaced, and the contents of the cell thoroughly mixed by inverting the cell six times. The cell was then replaced in the cell-holder, an initial reading taken, and further readings taken at suitable time-intervals, at the chosen wavelength. The minimum time between readings with this method was 5 s.

Calculation of Rate Constants.—The first-order rate equation applied to the present case takes the form (xiii), or (xiv), derived from the integrated form of equation (ix), where E_0, E_t, and E_∞ are the absorbance values at zero time,

$$k_t = \ln\,[(E_\infty - E_0)/(E_\infty - E_t)] \qquad \text{(xiii)}$$

$$E_t = E_\infty - \exp\,[\ln\,(E_\infty - E_t) - kt] \qquad \text{(xiv)}$$

time t, and infinite time, respectively. Because of the experimental difficulty of measuring E_0 and E_∞ with precision, we have chosen to regard equation (xiv) as an equation in three unknowns, E_0, E_∞, and k. We have then to find values of these quantities which most closely reproduce the observed dependence of E_t upon t.

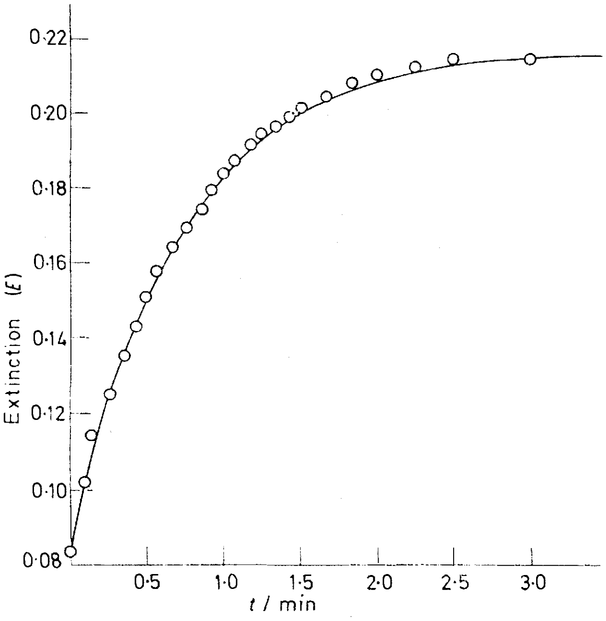
The equation, which is non-linear in the unknowns, is transformed into a linear form by replacing these quantities by guessed or estimated values $\hat{E}_0$, $\hat{E}_\infty$, and $\hat{k}$, and their deviations ΔE_0, ΔE_∞, and Δk from the true or ' best ' values. Thus $E_0 = \hat{E}_0 + \Delta E_0$, and similarly for E_∞ and k. The

$$\begin{aligned} E_t &= \phi(E_0, E_\infty, k) - \phi(E_0, E_\infty, k) \\ &= \frac{\partial\phi(E_0, E_\infty, k)}{\partial E_0}\,\Delta E_0 + \frac{\partial\phi(E_0, E_\infty, k)}{\partial E_\infty}\,\Delta E_\infty + \\ &\qquad \frac{\partial\phi(E_0, E_\infty, k)}{\partial k}\,\Delta k \qquad \text{(xv)} \end{aligned}$$

function is then expanded in a Taylor series, giving a new function which takes the form (xv), to terms of the first order. Equation (ix) is then solved for ΔE_0, ΔE_∞, and Δk by the method of least squares. The values so obtained are used to provide new and better estimates of the unknowns. These are re-inserted into equation (ix) and the cycle is repeated until the calculated corrections are negligibly small.

Convergence was found to be rapid, and was stable with respect to the normal range of uncertainty associated with the initial estimates of the unknowns. The Figure shows, for a typical kinetic run, observed readings and the calculated curve obtained using this procedure.

Preparative Rearrangements.—1-Phenylprop-2-en-1-ol (2·0 ml) was added to a solution of the catalyst in sulpholan (30 ml), and the mixture kept at 35°. The initial straw colour usually changed to brown. N-Sodium hydrogen carbonate (30 ml) was then added, the mixture shaken, and then extracted with ether. The combined extracts were washed with water, dried ($MgSO_4$), and evaporated. The residue was then examined (a) by u.v. spectroscopy, (b) by g.l.c., using a column of Apiezon L on Celite, and (c) by mass spectrometry.



Variation of extinction (at 284 nm) with time for the anisotropy of 1-phenylprop-2-en-1-ol ($1·5 \times 10^{-4}$M) catalysed by $SnCl_4$ ($1·13 \times 10^{-4}$M) at 35° (the curve is computed)

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