Kinetic and Theoretical Considerations in the Hydrolysis of Iminocarbonates

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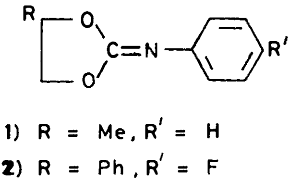
Analysis of the pH–rate profiles for the hydrolysis of 4-methyl-2-(*N*-phenylimino)-1,3-dioxolane (**1**) and 2-[*N*-(*p*-fluorophenyl)imino]-4-phenyl-1,3-dioxolane (**2**) together with product distribution of compounds (**1**)—(**5**) and p*K* values estimated for the various ionic forms T^0, T^+, $T^\pm$, and T^- of the tetrahedral intermediates, enables the determination of the reactivity of the tetrahedral intermediates along their reaction pathways. At pH <6, the only products formed are the amine and the carbonate (C–N fission) and at pH >6 C–O bond fission increases to form carbamates. The transition point corresponds to p*K* values of 9.2 and 8.5 for compounds (**1**) and (**2**), respectively. It is proposed that in acidic solution C–N bond fission proceeds *via* $T^+ \rightleftharpoons T^\pm \longrightarrow P$ while at a moderate pH this bond fission proceeds *via* a proton-switch mechanism $T^0 \longrightarrow T^\pm$. At pH >11 the only product produced is the hydroxycarbamate (C–O fission) *via* its anionic intermediate T^-. Mono- and gem-dimethyl substituted iminocarbonates T^- undergo two modes of ring-opening. Employing MNDO/H calculations the relative stability (ΔH_F) of the intermediates and their formed products was predicted and correlated with actual experimental product distribution.

Understanding the kinetic and thermodynamic parameters affecting the cleavage pattern of heteroatom bonds in monocyclic and acyclic systems is of great importance in predicting product distribution in a variety of chemical and biochemical processes. These parameters also play a central role in the partitioning modes of tetrahedral intermediates formed during nucleophilic attack on carbonyl groups. Along these lines, numerous studies on the hydrolysis or aminolysis of esters,[1–9] amides,[10–18] carbonates,[19–24] imidate esters,[25–32] thioacetals,[33–35] ortho esters,[36–38] amidoacetals,[39–42] amidines,[43,44] iminolactones,[45] imines,[46–53] oxazolidines,[54–57] and acetals[58–61] have been carried out during the last two decades. These studies indicated several important features affecting the product formation pathway: (a) the ionization state of the tetrahedral intermediate species, (b) the relative lifetime of the tetrahedral intermediates, (c) the leaving ability of the heteroatoms (kinetic control), (d) thermodynamic stabilities of the formed products, and (e) stereoelectronic control.[62]

We have demonstrated[20] that the preferred mode of ring opening in the aminolysis or basic hydrolysis of monosubstituted cyclic carbonates correlates with the pK_α values of their endocyclic oxygens, as presented in Scheme 1.

Since common intermediates may be formed during the aminolysis of carbonates and the hydrolysis of iminocarbonates, it is of general interest to compare kinetic features of the two systems. The present work describes the pH profiles of two iminocyclic carbonates: 4-methyl-2-(*N*-phenylimino)-1,3-dioxolane (**1**) and 2-[*N*-(*p*-fluorophenyl)imino]-4-phenyl-1,3-dioxolane (**2**) and the product distribution pattern of compounds (**1**)—(**5**).



(**1**) R = Me, R′ = H
(**2**) R = Ph, R′ = F
(**3**) R = p—ClC$_6$H$_4$OCH$_2$, R′ = H
(**4**) R = Ph, R′ = H
(**5**) R = Ph, R′ = Cl

Results

Kinetic Studies.—Hydrolysis of iminocarbonates (**1**) and (**2**) was studied at 60 °C in aqueous media over a pH range of 0.58—13.3 and ionic strength of 0.8M-KCl. Figure 1 shows the pH dependence of the pseudo-first-order rate constants (k_0) extrapolated to zero buffer concentration: The pH profile of amine formation is presented in Figure 2. At low pH, hydronium ion catalysis is observed (k_H). A pH-independent reaction is observed in the range pH 6—11 and pH 5—11 for compounds (**1**) and (**2**), respectively. At pH values greater than 11, hydroxide ion catalysis is apparent.

The pH-independent hydrolysis can also be attributed to the attack of water on the protonated iminocarbonate followed by the dissociation of H^+, [k_1 (H_2O)] or, alternatively, to the attack of water on the unprotonated iminocarbonate. According to Scheme 1 the course of the reaction can be expressed by equation (1):

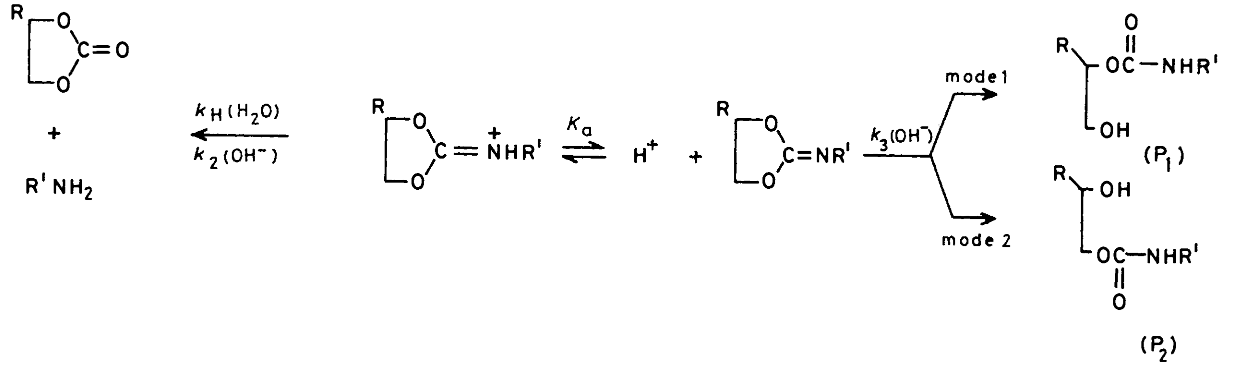
$$k_{\text{obs.}} = \frac{k_H[H^+] + k_2K_w + k_3K_a[^-OH]}{K_a + [H^+]} \qquad (1)$$

since in neutral or basic pH, $K_a \gg [H^+]$, equation (1) reduces to (2).

$$k_{\text{obs}} = \frac{k_H[H^+]}{K_a + [H^+]} + \frac{k_2K_w}{K_a} + k_3[^-OH] \qquad (2)$$

The data shown in Figure 1 fit equation (2) well. The apparent pK_a values and rate constants were found to be pK_a 2.85, k_H 0.26 min^{-1}, k_2 7.38 × 10^7 dm^3 mol^{-1} min^{-1}, k_3 0.146 dm^3 mol^{-1} min^{-1} for compound (**1**) and pK_a 2.73, k_H 0.245 min^{-1}, k_2 3.87 × 10^7 dm^3 mol^{-1} min^{-1}, and k_3 0.166 dm^3 mol^{-1} min^{-1} for compound (**2**).

Table 1 shows the distribution of products of three pH values as determined by ^{1}H n.m.r. Hydrolysis in acidic solutions yields



Scheme 1.

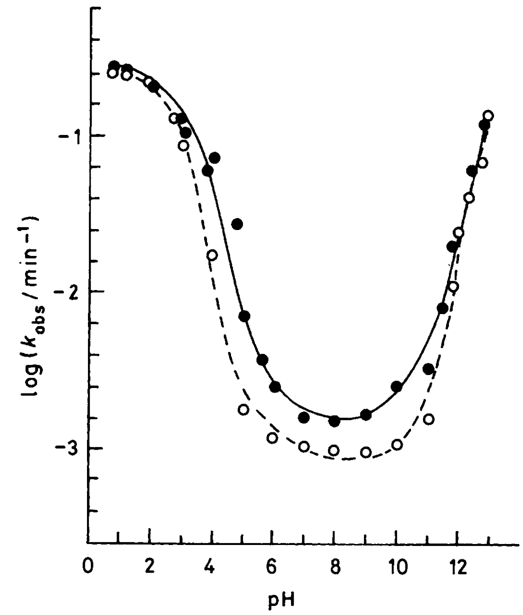


Figure 1. pH–rate profile of compound (**1**) (●——●) and (**2**) (○--○), at 60 °C, ionic strength 0.8M-KCl. The curves were calculated according to equation (2)

Table 1. % Amine and carbamate formed during the hydrolysis of cyclic iminocarbonate at various pH values

pH Product	1.0 Amine[a]	5.2 Amine[a]	11.3 Carbamate	
			mode 1	mode 2
Compound				
(**1**)	100	100	65	35
(**2**)	100	100	30	70
(**3**)	100	100	40	60
(**4**)	100	100	35	65
(**5**)			30	70

[a] Iminocarbonate hydrolysed to amine and cyclic carbonate

aniline and carbonate while, in basic solution, the results correlate well with the product distribution observed in the aminolysis of cyclic carbonates (modes 1 and 2 in Scheme 1). The product–pH profile for compounds (**1**) and (**2**) is given in Figure 2.

Estimation of p*K Values.*—The estimation of the p*K* values for the various ionic species T^0, T^+, $T^\pm$, and T^- (Scheme 2) was derived from their correlation with several reference compounds and in general by following a modified procedure of Fox and Jencks[63] (see also refs. 1, 13, 46, 59, and 66). ρ_I Used for the dissociation of alcohols was 8.4.[63] This is outlined in Tables 2 and 3.

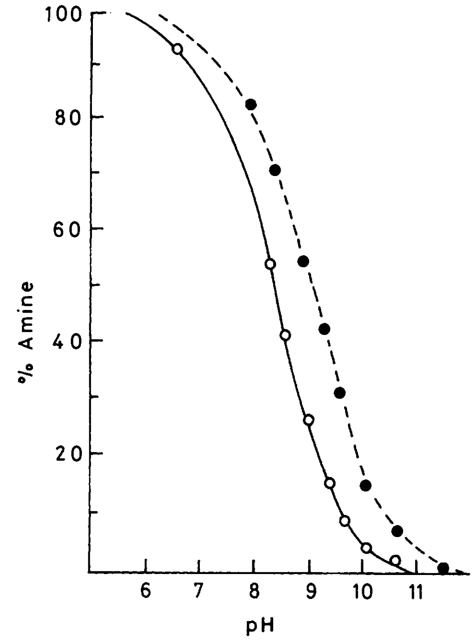
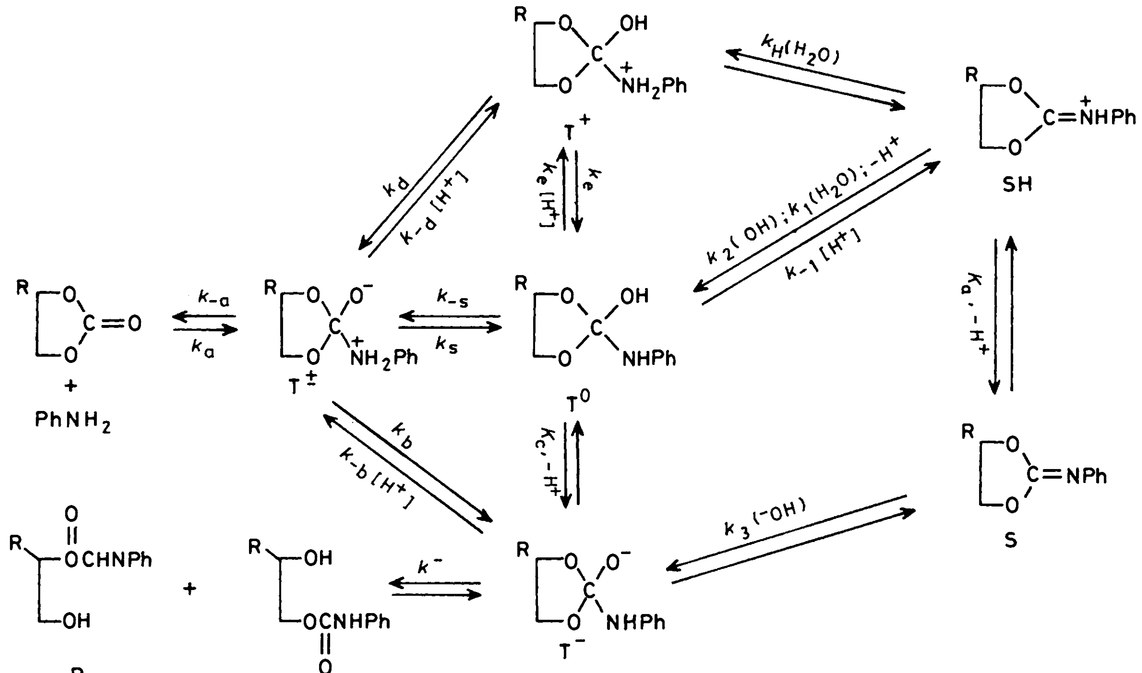


Figure 2. Amine yield as a function of pH in the hydrolysis of compounds (**1**) (●--●) and (**2**) (○——○)

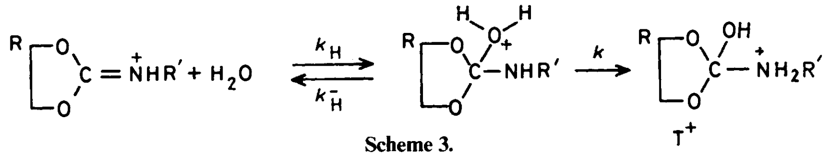
Discussion

Reaction Mechanism.—Since the aminolysis of cyclic carbonates and the basic hydrolysis of iminocarbonates [compounds (**1**)—(**5**)] result in a similar pattern of product distribution, it can be assumed that, along the course of both reaction pathways, some common intermediates are formed. In addition, the p*K* of the product transition curve, deduced from the product–pH profile (Figure 2), is about 4.6 and 3.9 p*K* units greater than the values of the anilinium leaving groups of compounds (**1**) and (**2**) respectively. This observation indicates that in addition to the anilinium ion, some other species are involved.

Analogous to imidate esters, Schiff bases, and amides, hydrolysis of iminocarbonates can be described according to the

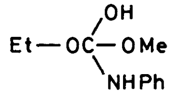
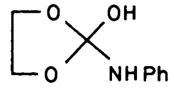
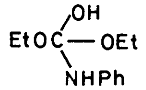
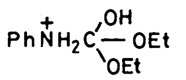
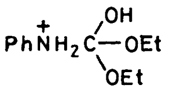


Scheme 2.



Scheme 3.

Table 2. Estimation of p*K* values (refer to Scheme 2 and Table 3)

pK_c (T^0 ⇌ T$^-$)	
 $EtOC(OH)(OMe)NHPh$	(f) − (III) + (VII) − (I) + (VI) = 10.06
	(g) − (II) + (VII) − (I) + (VI) = 9.86 (h) − (III) + (VI) = 9.09 − 10.09
 $EtOC(OH)(OEt)NHPh$	(a) + (VII) + (VII) + (VI) = 9.79
	Aver. 9.83
pK_e (T$^+$ ⇌ T^0)	
 $Ph\overset{+}{N}H_2C(OH)(OEt)OEt$	(i) + (VIII) + (VII) + (VII) = −0.45
pK_d (T$^+$ ⇌ T$^\pm$)	
 $Ph\overset{+}{N}H_2C(OH)(OEt)OEt$	*k* − (II) + (III) + (VII) + (VII) = 4.68
pK_b (T$^\pm$ ⇌ T$^-$)	
pK_c + pK_e = pK_d + pK_b; pK_b = 4.7	

general features discussed by Satterthwait and Jencks[1,27] as depicted in Scheme 2. Scheme 2 demonstrates the various ionic species involved in the hydrolysis and product formation of iminocarbamates.

Although Scheme 2 does not indicate which is the rate-limiting step, it is possible to predict the predominant reaction pathway. As evidenced in the hydrolytic pathways of imines[48,49] and imidate esters,[27,29] at very high acidity product

Table 3. Data relevant to Table 2

pK values for reference compounds		
	pK	Ref.
(a) Methanol	15.54	59, 64
(b) 1-Hydroxy-1-ethoxymethane	13.56	59
(c) Methanediol	13.27	59, 65
(d) Ethanol	16.0	59
(e) 2-Hydroxy-1,3-diphenylimidazolidine	12.75	63, 67
(f) α,α-Dihydroxy-α-methoxytoluene	10.7	68
(g) 1,1-Dihydroxy-1-methoxyethane	11.8	65
(h) 2-Hydroxy-2-phenyl-1,3-dioxolane	10—11	61
(i) Anilinium	4.85	32
(k) $CH_3\overset{+}{N}H_2CH_2OH$	9.98	63

Contribution to pK of various groups			
		Contribution to pK	Source
(I)	OH	−2.27	(a) − (b)
(II)	Me	+0.46	(d) − (a)
(III)	Ph	−0.84	$\sigma_I = 0.1$; $\rho_I = 8.4$; ref. 63
(IV)	MeN	+0.3	ref. 63
(V)	$PhNHCH_3$	−1.51	$\sigma = 0.18$; $\rho = 8.4$; ref. 66
(VI)	$PhNH_2$	−1.75	(V) − (IV) = −1.81 (e) − (a)/(2) − (IV) = −1.70
(VII)	EtO	−2	(b) − (a)
(VIII)	CH_2OH	−1.3	ref. 63

formation proceeds *via* intermediate T^+. According to Scheme 2, T^+ can be formed by: (a) water attack on the protonated iminocarbonate followed by fast proton transfer within the encounter complex (Scheme 3). Since the proton-transfer step is thermodynamically favoured, ($k > k_H$), k_H is therefore the rate-limiting step. (b) General base-catalysed attack by water, $[k_1(H_2O)]$ or nucleophilic ^-OH attack on the protonated iminocarbonate ($k_2[^-OH]$), to form the neutral tetrahedral intermediate T^0, followed by the thermodynamically favourable protonation step ($k_e[H^+]$).

Since $k_e[H^+] > k_{-1}[H^+]$ ($k_{-1}[H^+]$ involves protonation and carbon–oxygen bond-breaking) the rate-determining step for water attack and for hydroxide ion attack is $k_1(H_2O)$ and $k_2(^-OH)$, respectively. According to Scheme 2, the formation of carbonate and amine results only from the intermediate $T^\pm$. With aliphatic amines, the expulsion rate (k_{-a}) of RNH_3 or R_2NH_2 from $T^\pm$ intermediates in the hydrolysis of esters or amides was estimated to be in the range of 10^7—10^9 s^{-1}.[2,10,27] Since proton transfer in the k_{-d} direction is thermodynamically favoured, the rate in highly acidic solution should approach a diffusion control rate of *ca.* 10^{10} dm^3 mol^{-1} s^{-1}. Under these conditions where $k_{-d}[H^+] > k_{-a}$ ($> k_s$), the product-determining step is the breakdown of $T^\pm$. This is probably not the case with anilinium or *N*-methylanilinium as leaving groups. The leaving ability of these ions is at least three orders of magnitude faster than the alkylammonium cations.[39] Thus k_{-a} would reach a value greater than the diffusion control limit. This implies that the product-determining step for the anilinium ion and carbonate should be the formation of $T^\pm$ *via* proton transfer from T^+ to H_2O. As acidity is decreased, the formation of $T^\pm$ *via* a proton switch k_{-s} becomes favourable over its formation through the relatively stable T^+ intermediate.

At pH 4—6.5, the uncharged T^0 intermediate is the major species in solution. Since the neutral intermediate is not capable of expelling leaving groups for which the pK of the conjugated acid is greater than 10—12,[25] the products pathway (pH 4—6.5) proceeds *via* the proton switch mechanism (k_{-s}). Then amine expulsion is highly favoured.

For methyl formate and hydrazine, and for 2-hydroxymethylbenzamide, the ratio of C–N *vs.* C–O bond cleavage from intermediate T^0 was estimated to be 220 and 59, respectively.[69] Supporting data for the low leaving ability of ROH from the neutral tetrahedral intermediate is also obtained from the rates and equilibrium constants of hemiorthoesters and hemiacetal formation.[39b] The rate of the uncatalysed decomposition of 2-hydroxy-2-phenyl-1,3-dioxolane is only 1.5 s^{-1}, while second-order specific base catalysis of decomposition is 6×10^{10} s^{-1} M^{-1}. A further indication for the above partition preference from neutral intermediate T^0 is given in Table 1. At pH 5.2, T^0 prevails in high concentration and the amine yield is 100%.

At pH >6.5 the yield of amine and carbonate (C–N fission) decreases and, gradually, the amount of C–O bond fission to yield carbamates increases. The product transition point corresponds to a pK of 9.2 and 8.5 for compounds (**1**) and (**2**), respectively. Alkoxide departure becomes favourable from T^- intermediate, and thus product partition in the pH range 6.5—11 depends on both T^0/T^- and k^-/k_{-s} ratios. The variation in amine yield is given by equation (3).

$$\text{Amine yield} = \frac{[H^+]}{k^- K_c/k_{-s} + [H^+]} \qquad (3)$$

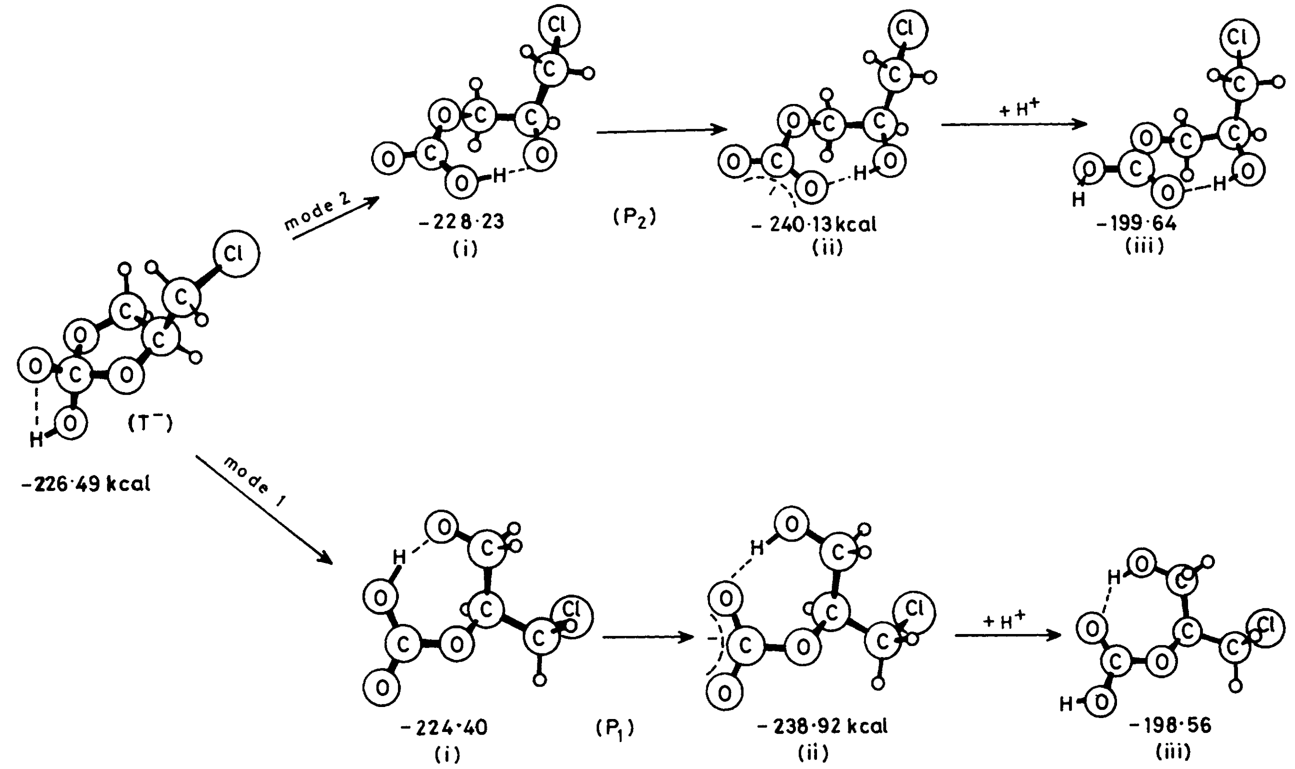
Since for compound (**1**): $-\log(k^- K_c/k_{-s}) = 9.2$ and pK_c = 10, a value of $k^-/k_{-s} = 4.3$ is obtained. From the dissociation constants (pK_e, pK_d, pK_c, and pK_b), the ratio $T^0/T^\pm = k_s/k_{-s} = K_s$ is estimated to be $\sim 10^6$. This value is in accord with the value $K_s = 1.58 \times 10^6$ predicted for the ratio formed in the case of *N*-methyl-*N*-phenylacetimidate.[66]

Since the maximal value of k_s is estimated to be in the range 10^6—10^8,[70] it implies that $k_{-s} \leq 100$ s^{-1} and, thus, the limiting rate for alkoxide expulsion from T^- is then $k^- \leq 430$ s^{-1}. This value is much lower than 2.5×10^7 s^{-1} and 79×10^4 s^{-1} estimated for 2-hydroxy-2-phenyl-1,3-dioxolane[61] and *N*-(α-ethoxyethylidene)-*N*-methylanilinium ion,[66] respectively.

At pH > 11, the only product produced is hydroxycarbamate. Under alkaline conditions, the anionic intermediate T^- can be formed directly from the non-protonated iminocarbonate by specific base catalysis (k_3). This intermediate (T^-) seems to be the predominant species in the aminolysis of cyclic carbonates at basic conditions. The similarity in product distribution (hydroxycarbamates) results from the hydrolysis of monosubstituted cyclic iminocarbonates and from the aminolysis of the analogous cyclic carbonate esters supports this suggestion.

In a stepwise mechanism, general base catalysis (k_b) is the main route for the conversion of $T^\pm$ into T^-. With basic amine, the lifetime of the initially formed $T^\pm$ is sufficient for proton transfer to a catalyst within the encounter complex. However, in the case of a weak base such as aniline, the reverse reaction k_{-a} is in the range of the diffusion control rate, T^- is less stable, and proton abstraction by catalyst becomes insignificant within the encounter complex of preassociated reactants and catalysts. Indeed, aniline does not react with cyclic carbonate to form hydroxycarbamate but if the aniline entity is already part of the molecule as is the case of compound (**1**), the reaction prevails.

The relatively small rate constant for the upper limit of alkoxide expulsion $k^- = 630$ s^{-1} is in accord with rate-determining step of the leaving group departure or alternatively with a



Scheme 4.

late transition state. The equilibrium constant K_3(S $\overset{^-OH}{\rightleftharpoons}$ T$^-$) is estimated to be $K_3k^- = 0.16/60$; $K_3 = 4.2 \times 10^{-6}$ dm^3 mol^{-1} which corresponds with the rate-determining step of leaving group expulsion. In order for the nucleophilic attack of hydroxide ion on (S) to become rate determining ($K_3 < 1$) the proton switch rate k_S should reach a value of less than 4.2×10^2 s^{-1}. This value is considered improbable for a thermodynamically favoured rate.

If, in the hydrolysis of S, the breakdown rate of the T$^-$ and not its formation is kinetically significant, the transition state of the reaction is then considered to resemble the products (late transition state). It can therefore be assumed that the amount of ring cleavage *via* mode 1 and mode 2 can be predicted from the relative stabilities (ΔH_F) of the products. Since heat of formation values (ΔH_f) can be obtained from MNDO calculations, we tested the correlation between the calculated energy of the products and the experimental results of product distribution.

ΔH_F Calculations of Anionic Intermediate (T$^-$) *and Products* (P_1, P_2).—It was previously demonstrated[20] that product distribution in basic conditions is not affected by the nature of the nucleophile (amine *vs.* hydroxyde ion). In the aminolysis and alkaline hydrolysis of cyclic carbonates or in the basic hydrolysis of iminocarbonates, similar products were obtained. Thus, for quantum mechanical calculations of these reactions we have chosen to calculate the product formation pathways starting from the anionic intermediate produced *via* $^-$OH attack on cyclic carbonates. These calculations do not take into consideration the stabilizing effect of water on the ionized species, and are of the 'gas phase' type. The energetics calculated relate to alternative pathways having parallel structural components, and the solvent stabilization is tentatively assumed to be equal for parallel species. This assumption should also hold for H-bonded species calculated; an intramolecular H bond which is stronger in one species may be replaced in water, by a stronger H bond to H_2O.

Scheme 4 shows the optimized structures and the heats of formation (ΔH_F) for the ionic species (i)—(iii) formed *via* mode 1 and mode 2 ring-opening of the anionic tetrahedral intermediate (T$^-$) of monosubstituted five-membered-ring cyclic carbonate.

Form (i) represents the less stable products (P_1, P_2) in which the proton is located on the less basic oxygen (*i.e.* the carbonate oxyanion). Thermodynamically favourable proton transfer to the more basic alkoxide anion leads to the preferred product (ii). Scheme 4 involves a stepwise formation of (ii); however, a concerted pathway, where C–O bond breaking proceeds simultaneously with proton transfer, can also be operative.

From the ΔH_F difference of the respective products formed in the two modes of reaction, the relative amount of P_1 and P_2 for both species (i) and (ii) were calculated for some selected carbonates (Table 4).

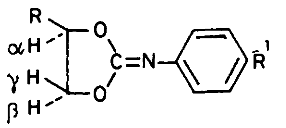
It is apparent that in the case of compounds (**6**), (**7**), and (**9**), product distribution calculated from $\Delta\Delta H_F$ values of (ii) correlate well with the experimental data. The calculated ΔH_F values of T$^-$ (i) and (ii) also indicate that if the transition state of alkoxide expulsion from T$^-$ resembles the products, a concerted pathway of proton transfer from the hydroxy group of T$^-$ to the leaving alkoxide ion is preferred over a stepwise mechanism. The gain in energy $\{[\Delta H(\text{ii}) - \Delta H(\text{T}^-)] - [\Delta H(\text{i}) - \Delta H(\text{T}^-)] = \Delta H(\text{ii}) - \Delta H(\text{i})\}$ by direct formation of (ii) (concerted) compared to the formation of (i) is 11.4, 9.55, 14.57, and 14.63 kcal for (**6**), (**7**), (**8**), and (**9**), respectively (mode 2) and 14.52, 13.85, 14.45, and 9.17 kcal for the corresponding compounds, obtained *via* mode 1 reaction.

In addition, it can be seen that the formation of (i) *via* mode 1 is thermodynamically unfavourable. The products (P_1) are of higher ΔH_F values than the starting T$^-$ intermediates. $\Delta H(P_1)(\text{i}) - \Delta H(\text{T}^-)$ values for (**6**)—(**9**) are calculated to be 2.09, 0.34, 0.22, and 1.97 kcal respectively. This is not the case for

Table 4. Calculated and experimental percentages of product distribution formed from anionic intermediate (T^-) according to Scheme 2

	$-\Delta H_f$/kcal mol^{-1}			% P_2, P_1 (calculated)			% P_2, P_1 (calculated)			% P_2, P_1 (found)		
	T^-	P_2	P_1	$\Delta\Delta H^a$ (i)	P_2	P_1	$\Delta\Delta H^a$ (ii)	P_2	P_1	P_2	P_1	$\Delta\Delta H^a$ (iii)
(**6**) R = CH_2Cl		228.23 (i)	224.40 (i)	−3.8	99.8	0.2						
R′ = H	226.49	240.13 (ii)	238.92 (ii)				−1.21	89	11	80	20	
		199.64 (iii)	198.56 (iii)									−1.08
(**7**) R = Ph		180.72 (i)	212.86 (i)	−1.13	87	13						
R′ = H	179.98	190.90 (ii)	193.44 (ii)				−0.46	68	32	70	30	
		156.53 (iii)	157.83 (iii)									+1.2
(**8**) R = Me		212.86 (i)	213.11 (i)	+0.25	40	60				40	60	
R′ = H	212.89	227.43 (ii)	227.12 (ii)				−0.31	63	37			
		192.05 (iii)	192.51 (iii)									+0.46
(**9**) R = Me		211.37 (i)	210.63 (i)	−0.74	78	22						
R′ = Me	212.60	226.02 (ii)	223.74 (ii)				−2.28	98	2	100	0	
		190.36 (iii)	189.98 (iii)									−0.38

^{a} $\Delta\Delta H = \Delta H(P_2) - \Delta H(P_1)$.



direct formation of P_1(ii) in which the concerted proton-transfer step pushes the reaction downhill.

Product distribution affected by *gem* dimethyl substituents were noted to be also in good correlation with $\Delta\Delta H_f$ of (ii). Since the leaving ability of oxyanion *via* mode 2 in the latter case is smaller than that *via* mode 1, we previously[20] explained the exclusive preference of ring opening *via* mode 2 in terms of product conformation. In light of the present calculations, it seems that the expulsion of the more basic alkoxide ion (mode 2) is energetically favoured when a proton-transfer step is involved. The formation of (i) *via* both modes is thermodynamically unfavoured [ΔH(i) − ΔH(T^-) are 1.97 and 1.23 kcal for P_1(i) and P_2(i) respectively]. It is noteworthy that the product distribution of (**8**) fails to agree with $\Delta\Delta H$(ii) but does so with $\Delta\Delta H$(i).

Table 4 also includes values of $\Delta\Delta H_F$(iii) which were evaluated for the protonated species of (i) or (ii). Kinetically, this is equivalent to the breakdown of the non-ionic intermediate T^0 in a non-catalytic reaction. However, the values of $\Delta\Delta H_F$(iii) indicate that if alkoxide expulsion is subject to general acid catalysis or if the basicity of solution is gradually reduced, the preferred mode of reaction tends to decrease while the second mode increases. This tendency of reaction has been experimentally shown.[20]

Under neutral or acidic conditions carbonate ions are known to undergo (spontaneous) decarboxylation and the only product formed *via* the two pathways of ring opening is the diol, so that the relative yields of P_2(iii) and P_1(iii) cannot be determined and compared with the theoretical results.

Experimental

Preparation of Iminocarbonates.—2-*N*-Arylimino-1,3-dioxolanes (iminocarbonates) were prepared[71—73] by treating the appropriate diol with the corresponding phenyl isocyanide dichloride. Phenyl isocyanide dichloride derivatives were synthesized according to the method of Murphy[74] and were sealed immediately in ampoules until used.

General procedure. NaH (2 equiv.) was added to a diol (1 equiv.) dissolved in dry dioxane kept under nitrogen. The solution was refluxed for 2 h, cooled to room temperature, and isocyanide dichloride (1 equiv.) in dioxane was added slowly. During the addition, the temperature was kept in the range of 20—25 °C. The solution was then refluxed for 2 h, the dioxane was distilled, and the crude material left was washed with water and extracted several times with benzene. The combined extract was dried over $CaCl_2$. After distillation of the benzene, the product was either distilled under low pressure or precipitated from ether or ether–light petroleum (b.p. 40—60 °C). I.r. measurements were recorded on a Perkin–Elmer model 457 spectrophotometer and n.m.r. spectra were recorded on a Bruker WH 300 spectrometer.

Phenyl isocyanide dichloride: colourless oil, b.p. 100—104 °C/25 mmHg (lit.,[74] 103—106 °C/31 mmHg); $\nu_{max.}$ 1 650, 1 595, 1 480, 907, 875, 700, and 570 cm^{-1}. *p*-Chlorophenyl isocyanide dichloride: oil, yellow-green, b.p. 136 °C/25 mmHg; $\nu_{max.}$ 1 650, 1 490, 900, 825, 620, and 540 cm^{-1}. *p*-Fluorophenyl isocyanide dichloride: colourless oil, b.p. 101—104 °C/25 mmHg (lit.,[71] 82—87 °C/ 11 mmHg).

4-*Methyl*-2-(N-*phenylimino*)-1,3-*dioxolane* (**1**), b.p. 124 °C/2 mmHg; $\nu_{max.}$ 1 710 (C=N) cm^{-1}; δ($CDCl_3$) 7.10 (Ph, 5 H, m), 4.65 (α, 1 H, m), 4.30 (β, 1 H, dd), 3.80 (γ, 1 H, dd), and 1.35 (Me, 3 H, dd); *m/z* 177 (M^+) and 119 (PhN=C–O) (Found: C, 67.51; H, 6.30; H, 8.24. Calc. for $C_{10}H_{11}NO_2$: C, 67.8; H, 6.22; N, 7.91%).

2-[N-(p-*Fluorophenyl*)*imino*]-4-*phenyl*-1,3-*dioxolane* (**2**), m.p. 85 °C; $\nu_{max.}$ 1 725 (C=N) cm^{-1}; δ($CDCl_3$) 7.35 (Ph, 5 H, s), 7.10 (ArH, 4 H, m), 5.6 (α, 1 H, t), 4.73 (β, 1 H, dt), and 4.28 (γ, 1 H, t); *m/z* 257 (M^+) and 137 (FC_6H_4NCO) (Found: C, 69.76; H, 4.75; F, 7.10; N, 5.61. Calc. for $C_{15}H_{12}FNO_2$: C, 70.04; H, 4.67; F, 7.39; N, 5.45%).

2-(N-*Phenylimino*)-4-*phenyl*-1,3-*dioxolane* (**4**), m.p. 64 °C; $\nu_{max.}$ 1 725 (C=N) cm^{-1}; δ($CDCl_3$) 7.30, 7.15 (Ph, 10 H, m), 5.52 (α, 1 H, t), 4.65 (β, 1 H, dt), and 4.19 (γ, 1 H, t); *m/z* 239 (M^+), 119 (PhNCO), and 91 ($C_7H_9^+$) (Found: C, 74.47; H, 5.34; N, 5.79. Calc. for $C_{15}H_{13}NO_2$: C, 74.7; H, 5.58; N, 6.01%).

4-*Chlorophenoxymethyl*-2-(N-*phenylimino*)-1,3-*dioxolane* (**3**), m.p. 113 °C; $\nu_{max.}$ 1 710 (C=N); δ($CDCl_3$) 7.10 (Ph, 5 H, m), 7.15, 6.80 (ArH, 4 H, AA′, BB′), 4.90 (α, 1 H, m), 4.45 (β, γ, 2 H, m), and 4.10 (δ, 2 H, m); *m/z* 305, 303 (M^+) (Found: C, 63.56; H, 4.66; Cl, 11.76; N, 4.46. Calc. for $C_{16}H_{14}ClNO_3$: C, 63.60; H, 4.62; Cl, 11.7; N, 4.62%).

2-[N-(p-*Chlorophenyl*)*imino*]-4-*phenyl*-1,3-*dioxolane* (**5**), m.p. 88 °C; $\nu_{max.}$ 1 725 (C=N) cm^{-1}; δ($CDCl_3$) 7.50 (Ph, 5 H, s), 7.30 (ArH, 4 H, m), 5.75 (α, 1 H, t), 4.83 (β, 1 H, dt), and 4.33 (γ, 1 H, t) (Found: C, 65.62; H, 4.59; Cl, 12.71; N, 5.03. Calc. for $C_{15}H_{12}ClNO_2$: C, 65.8; H, 4.38; Cl, 12.97; N, 5.11%).

Method

Heat of Formation (ΔH_F).—Semi-empirical SCF calculations were performed by MNDO[75] which was recently modified to handle correctly hydrogen-bonding interactions.[76,77] The corrected version, MNDO/H, is required for an appropriate description of reactants, intermediates, and products involved in the reaction pathways of this study.

Total geometry optimization, including internal rotations, was performed for each of the molecular species. Second derivatives were estimated for all $3N - 6$ geometrical parameters during optimization. The minima were verified through the second derivatives (Hessian) matrix eigenvalues, which must be all positive.

DFP[78] analytic gradients were used throughout the optimization. Entropies were calculated by evaluation of the vibrational, rotational, and translational partition functions.[79] As small differences were found between the entropies in each transformation scheme these values are not reported.

Kinetics.—All kinetic measurements were carried out at 60 ± 0.2 °C and ionic strength 0.8M-KCl. Reactions were followed by monitoring the u.v. absorbance change at 255 nm for the disappearance of the iminocarbonates and (in acidic solutions) at 283 nm for the appearance of aniline. Spectra and rates were obtained on Unicam SP 800 spectrophotometer. All observed rate constants were pseudo-first-order and were calculated using a non-linear least-squares analysis on a CDC 6400A computer. Buffer concentrations were in the range of 0.02—0.1M and rates used for the pH-rate profile were obtained by extrapolation of the first-order reaction rates to zero buffer concentration. Reactions were initiated by adding 10—20 μl of the substrate in acetonitrile to 3 ml of buffer in a quartz cell incubated in the cell holder of the spectrophotometer.

Product analysis was determined either by direct spectrophotometric examination of products mixture aniline and hydroxycarbamates and by means of the n.m.r. method as previously described[20] for the ring opening of cyclic carbonates.

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