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THEORETICAL STUDIES ON THE ACID-CATALYSED AROMATIZATION OF BENZENE-*cis*-1,2-DIHYDRODIOLS*

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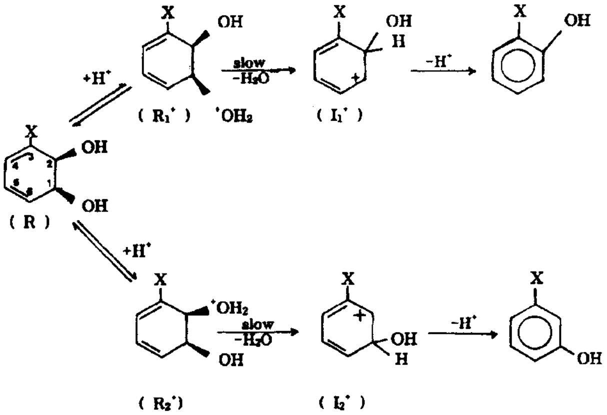
Theoretical studies on the acid-catalysed dehydration of 15-substituted dihydrodiols were carried out using the AM1 method. In agreement with the experimental results, the rate-limiting step is dehydration of the protonated diols, R^+, and the *o*-phenol-forming pathway (path 1) is favoured both kinetically and thermodynamically over *m*-phenol product formation. The transition state for path 1 (TS 1) is found to be at an early position (*ca* 23% progress) along the reaction coordinate and a better correlation of the rate constant is obtained with σ^+. Three resonance forms can exist for the benzenonium intermediate but the contribution of one form is dominant in the later TS, which resembles the cationic intermediate. The contribution of the other two, however, weakens the σ^+ effect of +M subsituents. The σ_p correlation of the rate constant in acid solution is therefore suggestive of a later TS resembling the cationic intermediate which is stabilized by solution.

INTRODUCTION

In the presence of acids, arene dihydrodiols undergo dehydration and aromatization to form phenols. Boyd *et al.*[2] have reported rate constants for the aromatization of a number of benzenedihydrodiols (R) in aqueous acid. They suggested that the rate-determining step in the dehydration reaction is generation of a carbocation intermediate, I^+, from the protonated diols, R^+ [equations (1) and (2)]. Rate measurements and product analysis in aqueous $HClO_4$ at 25 °C resulted in most cases in the predominant formation of the *o*-phenol (path 1).[2] For this process, a Hammett plot with $\rho = -8{\cdot}2$ was obtained with σ_p rather than σ^+ for +M resonance substituents such as Me and MeO. This was rationalized as a reaction proceeding via a benzenonium



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[*] Determination of Reactivity by MO Theory, Part 92. For Part 91, see Reference 1.
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ion-like intermediate[3] with a marked imbalance between resonance and inductive stabilization of the transition state (TS).[4]

In order to shed more light on the mechanism involved, we carried out AM1[5a] calculations on R, R^-, TS and I^+ forms with 15 Xs for paths 1 and 2, and offer correct interpretations of the experimental results obtained by Boyd *et al.*[2]

CALCULATIONS

The AM1 method was used throughout.[5b] All geometries were fully optimized and stationary point species including TS were confirmed by vibrational frequency calculations.[6]

RESULTS AND DISCUSSION

The heats of formation obtained are summarized in Table 1. We note that in agreement with the experimental results, path 1 is favoured over path 2 in all cases expect for $X = CF_3$.[2] The *o*-phenol-forming pathway (path 1) is preferred not only kinetically (lower $\Delta H^{\ddagger}$) but also thermodynamically (lower ΔH°). The barrier to the dehydration process is lower and the cationic intermediate, I^+, is more stable for path 1 than path 2.

Bond lengths and their changes involved in the activation process for the $C—OH_2^+$ and C-3—X bonds, i.e. $d(C—OH_2^+)$ and d(C-3—X) in R^+ and $\Delta d^{\ddagger} = d(TS) - d(R^+)$, are summarized in Table 2. The data reveal that $d(C—OH_2^+)$ in R^+ is longer but $\Delta d^{\ddagger}(C—OH_2^+)$ is smaller, especially with +M substituents, for path 1. This is consistent with the Kirby's rule[7] that in the S_N1 process the bond length of the cleaving bond is already longer in the reactant with an electron-donating substituent, e.g. +M substituent, so that a smaller extent of bond stretching is required in the TS and hence a lower barrier to dehydration is observed. In fact, for path 1, a good linear correlation ($r = 0·967$) exists between $\Delta H^{\ddagger}$ and $d(C—OH_2^+)$ with a negative slope (*ca* $-167·2$ kcal mol^{-1} Å^{-1}). The $\Delta H^{\ddagger}$ value can also be correlated ($r = 0·923$) with $\Delta d^{\ddagger}(C—OH_2^+)$ with a positive slope (*ca* 10·8 kcal mol^{-1} Å^{-1}). In accordance with the Bell–Evans–Polanyi (BEP) principle,[8] a straight-line relationship ($r = 0·920$) is also found for path 1 between $\Delta H^{\ddagger}$ and ΔH°:

$$\delta \Delta H^{\ddagger} = \alpha \delta \Delta H^{\circ} \qquad (3)$$

The slope obtained ($\alpha = 0·23$) is significantly low, indicating that the TS is reached in the early part (*ca* 23% progress) of the reaction coordinate.[9] This means that the TS resembles closely the starting species, R^+, in dehydration process (1). In agreement with this, d(C-3—X) is shorter in R^+ and further contraction in the activation process, $\Delta d^{\ddagger}$(C-3—X), is small (Table 2); significant bond contraction, $\Delta d^{\ddagger} < 0$, however, occurs for +M substituents.

In contrast to the experimentally observed correlation between log *k* and σ_p,[2] we now obtain a better straight-line plot for $\Delta H^{\ddagger}/2·3RT$ versus σ^+ (rather than versus σ_p) with a slope of $-2·4$ ($r = 0·93$), which is smaller than the corresponding value of $-3·0$ for the gas-phase

Table 1. AM1 heats of formation, ΔH_f, of R^+, TS and I^+, and enthalpies of activation $\Delta H^{\ddagger}$, and reaction, ΔH° (in kcal mol^{-1}; 1 kcal = 4·184 kJ)

		R^+		TS		$I^{+\,a}$		$\Delta H^{\ddagger}$		ΔH°	
X	σ_p^+	$R^{+\,b}_{(1)}$	$R^{+\,b}_{(2)}$	TS(1)[b]	TS(2)[b]	$I^{+\,b}_{(1)}$	$I^{+\,b}_{(2)}$	(1)[b]	(2)[b]	(1)[b]	(2)[b]
EtO	−0·82	57·27	62·16	58·39	68·86	54·29	71·91	1·12	6·70	−2·98	9·75
MeO	−0·78	63·80	68·82	65·13	75·22	62·14	78·69	1·33	6·40	−1·66	9·87
MeS	−0·60	103·06	106·94	104·52	110·55	94·89	113·54	1·46	3·61	−8·17	6·60
PhS	−0·45	134·19	138·43	135·15	140·95	123·71	142·28	0·96	2·52	−10·48	3·85
Me	−0·31	97·98	98·76	100·89	102·60	101·51	105·39	2·91	3·84	3·53	6·63
Et	−0·30	91·79	92·55	94·58	96·22	95·72	99·12	2·79	3·67	3·93	6·57
Ph	−0·18	129·95	132·94	132·27	135·45	129·19	137·22	2·32	2·51	−0·76	4·28
$CH_2{=}CH$	—	121·69	122·79	124·26	126·93	122·19	129·60	2·57	4·14	0·50	6·81
F	−0·07	64·82	68·08	68·01	74·20	70·25	78·05	3·19	6·12	5·43	9·97
H	0·0	106·93	—	110·86	—	114·54	—	3·93	—	7·61	—
Cl	0·11	102·64	104·13	106·43	109·13	109·33	112·85	3·79	5·00	6·69	8·72
Br	0·15	115·52	116·01	120·00	120·75	124·34	124·59	4·48	4·74	8·82	8·58
$HC{\equiv}C$	0·18	161·08	162·10	164·12	166·52	165·27	169·30	3·04	4·42	4·19	7·20
PhSO	0·50	102·67	98·29	108·16	107·37	111·94	112·49	5·49	9·08	9·27	14·20
CF_3	0·43[c]	−41·71	−40·48	−34·53	−35·19	−27·19	−30·20	7·18	5·29	14·52	10·28

[a] Heats of formation for $I^+ + H_2O$ (−59·24 kcal mol^{-1}).

[b] (1) and (2) denotes reaction paths 1 and 2, respectively.

[c] σ_m Value.

Table 2. Bond lengths (d) in R^+ and their changes in the activation process, $\Delta d^{\neq}(= d^{\neq} - d_{R^+})$ (in Å)

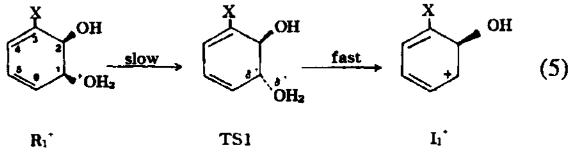
X	Path	$d(C—OH_2^+)$	$d(X—C\text{-}3)$	$\Delta d^{\neq}(C—OH_2^+)$	$\Delta d^{\neq}(X—C\text{-}3)$
EtO	1	1·574	1·360	0·218	−0·009
	2	1·509	1·375	0·532	−0·002
MeO	1	1·571	1·363	0·229	−0·009
	2	1·509	1·378	0·540	−0·001
MeS	1	1·563	1·671	0·236	−0·016
	2	1·539	1·690	0·504	−0·004
PhS	1	1·570	1·672	0·196	−0·016
	2	1·537	1·697	0·463	−0·008
Me	1	1·558	1·479	0·347	−0·004
	2	1·555	1·481	0·412	0·003
Et	1	1·560	1·488	0·343	−0·003
	2	1·556	1·490	0·401	0·003
Ph	1	1·562	1·458	0·307	−0·005
	2	1·549	1·462	0·410	0·000
$CH_2{=}CH$	1	1·558	1·451	0·319	−0·005
	2	1·553	1·453	0·423	0·004
F	1	1·555	1·347	0·349	−0·007
	2	1·538	1·352	0·493	0·002
H	1, 2	1·553	1·103	0·416	0·001
Cl	1	1·551	1·687	0·393	−0·010
	2	1·548	1·689	0·460	0·000
Br	1	1·548	1·866	0·438	−0·006
	2	1·552	1·865	0·457	0·001
$HC{\equiv}C$	1	1·557	1·404	0·351	−0·004
	2	1·550	1·404	0·435	0·001
PhSO	1	1·545	1·745	0·388	0·013
	2	1·508	1·726	0·519	0·027
CF_3	1	1·538	1·533	0·811	0·006
	2	1·538	1·528	0·432	0·006

S_N1 processes of protonated benzyl compounds with a neutral leaving group:[10]

$$YC_6H_4CH_2FH^+ \xrightarrow{\text{slow}} Y\overset{\delta+}{C_6H_4CH_2} \cdots \overset{\delta+}{FH} \xrightarrow{\text{fast}} YC_6H_4\overset{+}{C}H_2 + FH \quad (4)$$

where Y = *para* substituents.

By analogy, the correlation with σ^+ can be fractionalized as follows. In the R^+ and TS partial positive charge develops at C-1:



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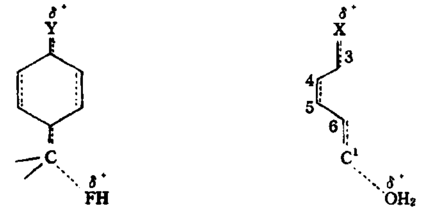
which act as an electron-deficient centre attached to C-6; thus the resemblance of the two TS structures is obvious (Scheme 1). In TS 1 a direct conjugation between +M substituents (X) and an electron-deficient centre bonded to the *para*-position (C-6) is possible (Table 3), so that the σ^+ effect prevails. The lower slope obtained (−2·4) than the corresponding slope for the benzylic system (−3·0) can easily be accounted for by a single π route of conjugation available for TS 1 in contrast to double π routes in the benzylic system. The direct conjugation afforded between X and C-1 in fact causes the C-1—$^+OH_2$ bond in R_1^+ to stretch a longer C-1—$^+OH_2$ bond permits a greater positive charge, i.e. a stronger electron-deficient centre, to be developed on C-1, leading to a greater resonance stabilization of R_1^+. The



benzylic system (eq. 4)   TS 1 (eq. 5)

Scheme 1

Table 3. Representative atomic charges, q, and their changes, Δq (= $q(Z) - q(R)$ where Z = R^+, TS or I^+), for reaction path 1 (in electronic charge units)

		q				Δq		
X		C-1	C-2	C-3	C-6	Δq(C-1)	Δq(C-3)	Δq(C-6)
MeO	R	0·077	0·045	0·015	−0·170			
	R^+	0·125	0·018	0·063	−0·315	0·048	0·048	−0·145
	TS	0·190	0·013	0·105	−0·313	0·113	0·090	−0·143
	I^+	−0·106	0·000	0·253	−0·161	−0·183	0·238	0·154
H	R	0·028	0·025	−0·194	−0·138			
	R^+	0·105	0·009	−0·175	−0·270	0·077	0·019	−0·132
	TS	0·213	−0·008	−0·100	−0·266	0·185	0·094	−0·128
	I^+	0·028	−0·021	0·028	−0·216	0·000	0·222	−0·078
F	R	0·074	0·018	0·010	−0·148			
	R^+	0·115	−0·009	0·055	−0·283	0·041	0·045	−0·135
	TS	0·208	−0·017	0·120	−0·281	0·134	0·110	−0·133
	I^+	−0·024	−0·014	0·274	−0·198	−0·098	0·264	−0·050
CF_3	R	0·062	0·050	−0·253	−0·136			
	R^+	0·094	0·034	−0·225	−0·241	0·032	0·028	−0·105
	TS	0·203	0·011	−0·090	−0·235	0·141	0·163	−0·099
	I^+	0·073	−0·003	−0·057	−0·218	0·011	0·196	−0·082

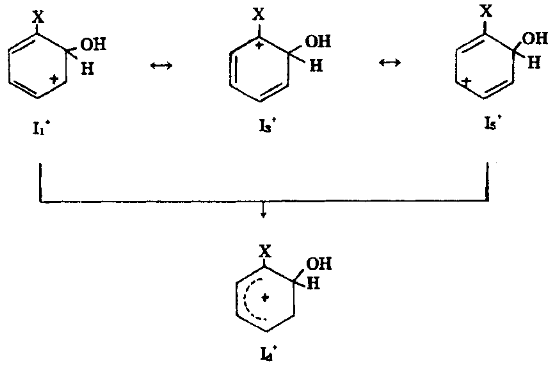
stronger the +M effect of X, the longer is the C-1—$^+OH_2$ bond in $R_1{}^+$ and the smaller will become the bond stretching required in the TS 1[7] (Table 2). In the $R_2{}^+$ and TS 2 structures [equation (2)], the cleaving H_2O is bonded to C-2, which in turn is attached to C-3 so that such direct conjugation of +M substituents with C-6 through π bonds is not possible.

Representative changes in the formal charge of some relevant atoms are shown in Table 3. the charge shift is seen to become stronger with the +M substituent (X = MeO) and decreases in the order X = MeO > F > H > CF_3. All other substituents studied in this work exhibited similar trend in the charge shift with the +M effect. We note that X = F acts as a weak π-donor (for F, $\sigma_p{}^+ = -0{\cdot}07$, indicating that F has a weak +M effect).

An interesting change to be noted is that in the benzenonium intermediate negative charge shifts from C-6 toward C-1 and substantial positive charge develops at the C-3 position. This suggests a significant contribution of resonance form $I_3{}^+$ to the benzenonium intermediate, especially for the strong +M substituent (Scheme 2). Resonance structure $I_3{}^+$ (and also $I_5{}^+$) counteracts the efficient resonance delocalization of +M substituents to the *para*-position, C-6; hence in the cationic intermediate the σ^+ effect will be much reduced (to *ca* one-third of $I_1{}^+$) owing to the contribution of resonance structures $I_3{}^+$ and $I_5{}^+$.

The two resonance structures, $I_1{}^+$ and $I_3{}^+$, of the benzenonium cation proposed by Boyd *et al.*[2] are incorrect. In fact, three resonance structures are possible (Scheme 2) and usually these three resonance structures are represented by a single form, $I_d{}^+$, in which the positive charge is delocalized over the entire ring excluding the C-2 atom, i.e. a σ-complex[11] formed by H^+ attack on C-2. Hence the substituent X is really at an *ortho*-position relative to this sp^3 centre formed by an electrophilic attack on C-2 by a cationic electrophile (H^+ in this case). Therefore, there seems to be no justification for using either σ^+ or σ_p constant in their argument based on the resonance structures $I_1{}^+$ and $I_3{}^+$.[2]

If the TS were structurally more similar to the benzenonium intermediate, i.e. if the TS occurred at a later position along the reaction coordinate,[8,9] the rate constant cannot be correlated with σ^+ owing to some contributions of the opposing resonance structures, $I_3{}^+$ and $I_5{}^+$, for +M substituents, but may be correlated with σ_p since the contribution of the $I_1{}^+$-like structure

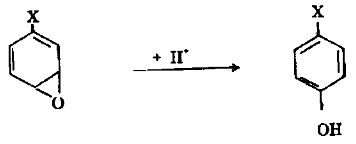


Scheme 2

will be stronger than that of the two opposing $I_3{}^+$- and $I_5{}^+$-like structures in the TS. In other words, in the TS the benzenonium intermediate is not fully developed yet and the contribution of the $I_1{}^+$-like structure will be dominant.

We conclude that in the gas phase (as theoretically found) the TS is located at an earlier position along the reaction coordinate (*ca* 23% progress of the reaction from R^+ to I^+), which is remote from the cationic intermediate, and the contributions of resonance structures $I_3{}^+$ and $I_5{}^+$ are insignificant so that the σ^+ effect prevails in correlating the rate constants [or, approximately, correlating the $-\Delta H^{\neq}/2{\cdot}3RT$ values (since $\delta \log k = -\delta\Delta G^{\neq}/2{\cdot}3RT$, by using $-\delta\Delta H^{\neq}/2{\cdot}3RT$ we are neglecting entropy effects)]. However for the reactions in aqueous acid solution, the TS may become shifted to a much later position along the reaction coordinate that the TS becomes more similar to the cationic intermediate, $I_d{}^+$, as a result of an efficient stabilization of the cationic intermediate by solvation (in aqueous solution, fully developed cationic charge in the benzenonium intermediate is expected to be more stabilized by solvation than the TS in which the positive charge is only partially developed on C-1 and shared between C-1 and the leaving group H_2O). The rate constant then can not be correlated by σ^+ but can still be correlated by σ_p because of the dominant contribution of $I_1{}^+$-like structure over the $I_3{}^+$- and $I_5{}^+$-like structures in the TS.

In acid-catalysed ring-opening of 4-substituted benzene oxides (BO) to form *para*-substituted phenols:[12]



(6)

(BO)

direct conjugation of +M substituents, X, is allowed to the *para*-position so that the rate constant can be correlated by σ^+.

We do not think, therefore, that the low resonance effect found experimentally[2] is due to an imbalance in the development of resonance and inductive effects.[4] It is merely due to the benzenonium-like (late) TS, which is a resonance hybrid, $I_d{}^+$, but is dominated by $I_1{}^+$, in which an electron-deficient centre at C-1 is bonded to the *para*-position (C-6) relative to +M substituents.

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