What Makes Hydrocyanic Acid a Normal Acid?

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A classical intersecting-state model is applied to the study of proton-transfer reactions of HCN with oxygen and nitrogen bases. According to theory, what makes these proton transfers fast processes is the involvement of the CN bond together with the XH bonds in the reaction co-ordinate, which increases the average bond order of the transition state and decreases the reaction energy barrier. The slow reactions of most carbon acids and the intermediate behaviour of some other carbon acids such as the malononitriles and ethyl vinyl ether are also discussed within this theoretical formalism.

Proton transfers from carbon acids are generally much slower than those from nitrogen and oxygen ones, which are essentially diffusion-controlled processes in the thermodynamically favourable direction. This slow proton transfer is currently attributed to changes in electron delocalization and hybridization accompanied by changes of the lengths and angles of bonds, poor hydrogen-bond donor–acceptor properties of carbon, and solvent reorganization.[1–3] However, recently, Bednar and Jencks[4] have studied several proton-transfer reactions of HCN and have concluded that this carbon acid behaves almost as a normal nitrogen or oxygen acid.

In order to study the intrinsic reactivity of a molecular species within a class of reacting systems one should assess the role of the thermodynamic factor, and compare the estimated intrinsic reactivities for the thermoneutral situation. Several molecular factors, such as bond lengths, force constants, and electronic properties, can play a role in the intrinsic kinetic reactivity. These factors are dealt with in models such as Marcus theory, frontier molecular orbital theory, configuration mixing model, resonance theory, and potential energy surface models, which, in many aspects, are mutually unrelated.[5] Recently we have developed a classical intersecting-state model (i.s.m.)[6] which seems to embrace all those models and several empirical correlations in a quantitative manner. When the effect of the reaction energy, force constants, and bond lengths is eliminated, proton-transfer reactivity can be assessed in terms of the concept of 'transition-state bond order' ($n^{\dagger}$). For the ionization reactions in water most carbon acids have $n^{\dagger}$ *ca.* 0.5, HF has $n^{\dagger}$ *ca.* 1.0, and nitrogen and oxygen acids have intermediate transition-state bond orders. As a consequence, the carbon 'pseudo acids' are kinetically less reactive with a behaviour close to radical-transfer type.[7] Although HCN is a carbon acid, its kinetic behaviour is extremely close to that of nitrogen and oxygen acids. It seems useful to apply i.s.m. to investigate the mechanism of proton transfer from HCN.

Theory

The theory has been described in detail elsewhere[6] and only the essential parts will be stated. For an intersecting-state model under the harmonic oscillator approximation, the transition state is found at the intersection of the potential energy curves of reactant and product, equation (1), where f_i are the stretching

$$\tfrac{1}{2}f_{\mathrm{r}}x^2 = \tfrac{1}{2}f_{\mathrm{p}}(d - x)^2 + \Delta G^{\circ} \qquad (1)$$

force constants of reactant and product, ΔG° is the reaction free energy, x is the bond distension of the reactant, and d is the sum of the bond distensions from reactant and product to the transition state. The parameter d is also the horizontal displacement of the two potential energy curves.

The activation free energy of the reaction is given by equation (2) where x is estimated from equations (1), once d is known.

$$\Delta G^{\dagger} = \tfrac{1}{2}f_{\mathrm{r}}x^2 \qquad (2)$$

The parameter d was shown[6] to be proportional to the sum of the equilibrium bond lengths of reactant and product ($l = l_{\mathrm{r}} + l_{\mathrm{p}}$), λ is a parameter with the dimensions of an energy which is associated with the 'mixing entropy' as defined by Agmon and Levine,[8] and a' is a constant ($a' = 0.156$) [equation (3)].

$$d = \left[\frac{a' \ln 2}{n^{\dagger}} + \frac{a'}{2}\left(\frac{\Delta G^{\circ}}{\lambda}\right)^2\right] l \qquad (3)$$

The proportionality between d and l has a simple meaning: when an equilibrium bond length is small its bond distension is small, but when it is large the bond distension is also large. At the transition state, the energy of the reaction should be considered as internal energy of the activated complexes and can be stored through further distension of the reactive bonds such that d increases. The magnitude of this effect depends on the availability of different ways of storing ΔG°, other than the reactive modes. This storing capacity is measured by λ. When $\lambda \gg |\Delta G^{\circ}|$ virtually no reaction energy is stored in the reactive modes and d is independent of ΔG°. This situation corresponds to the effect of ΔG° on $\Delta G^{\dagger}$ predicted by Marcus theory.[9] However, if $\lambda \gtrsim |\Delta G^{\circ}|$ a considerable amount of the reaction energy is stored in the reactive modes and d increases with an increase in $|\Delta G^{\circ}|$.

Results and Discussion

Configuration mixing models[5] show that the nature of the transition states can be strongly influenced by low-lying intermediate configurations. Let us consider two possible situations in an intersecting-state model: one where the transition state is a mixture of the configurations of the ground-state reactant and product, and the other where the transition state is dominated by the configuration of some intermediate configuration of low energy. As Figure 1 shows, the horizontal displacement of the potential energy curves is much smaller for the latter situation. We have shown[6] that the electronic characteristics of the transition state can be quantified in terms of the 'transition state bond order' ($n^{\dagger}$) and that d is inversely proportional to $n^{\dagger}$ when $\Delta G^{\circ} = 0$. For reactions involving a single bond in reactant ($n_{\mathrm{r}} = 1$) and a single bond in product ($n_{\mathrm{p}} = 1$) the conservation of the total bond order ($n_{\mathrm{r}} + n_{\mathrm{p}} = 1$) implies $n^{\dagger} = 1/2$ when $\Delta G^{\circ} = 0$. This situation corresponds to the case where the transition state is well represented by the configurations of reactant and product. However, when the transition state is represented by any intermediate configuration of a lower energy $n^{\dagger} > 1/2$.

The qualitative variation of the molecule orbital energies of

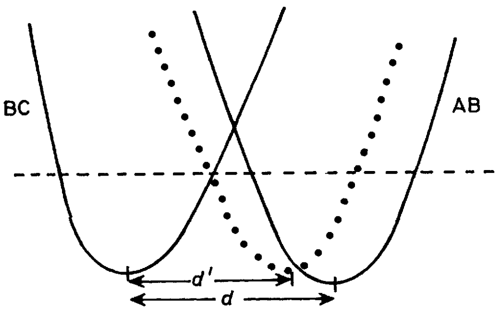


Figure 1. Intersecting-state diagram for a reaction A + BC ⟶ AB + C showing: (i) a transition state which is a mixture of reactant and product configurations with $n^\dagger = 1/2$ and a sum of bond distensions d; (ii) a transition state which is represented by an intermediate configuration of $n^\dagger > 1/2$ and a sum of bond extensions d'

triatomic molecules given by the diagrams of Walsh[10] reveals that the relative number of bonding and antibonding orbitals varies with the geometry of the molecule. For example, with XH_2 in a linear geometry the number of bonding (σ_s, σ_{p_z}) and antibonding (σ_s^*, $\sigma_{p_z}^*$) orbitals is the same. However, the number of bonding orbitals (σ_s, σ_{p_x}, σ_{p_z}) is higher than the antibonding orbitals for a nonlinear geometry, because the p orbital in the plane of the $\widehat{HXH}$ angle acquires a bonding character. This feature, which is valid in general for XY_2 molecules, seems to be important for the transition states with higher bond orders ($n^\dagger > 1/2$). For the reaction $H + HX \longrightarrow H_2 + X$ (X = halogen atom) the average transition-state bond order is $n^\dagger = 1$ and for $H + X_2 \longrightarrow HX + X$ is $n^\dagger = 1.5$. These transition-state configurations are not only associated with nonlinear geometries, but also with configurations of electronic excited states, because the electrons do not occupy the lowest molecular orbitals.[11] This last feature is agreement with similar suggestions from configuration mixing models.[5]

Reactions of HCN *with Bases.*—One of the possible mechanisms for the reaction of HCN with bases is the direct proton transfer (4) which can be thought to involve C–H and

$$B + HCN \longrightarrow BH^+ + CN^- \qquad (4)$$

B–H as the reactive bonds. For such a mechanism, we have shown that $n^\dagger \simeq 0.55$.[7] However, other reaction co-ordinates involving more than one bond in reactants and products can be considered. For example, reaction co-ordinate can involve two bonds in reactants, C–H and C≡N, and two bonds in products, B–H and C≡N. When the reaction co-ordinate involves bonds with a local mode character,‡ as is the case of HCN,[12] the effective force constant can be estimated as $f = (\Sigma f_i^2)^{\frac{1}{2}}$.[13] Although this reaction co-ordinate leads to an increase in f, it also leads to an increase in the transition-state bond order. The increase in $n^\dagger$ ($n^\dagger > 0.92$) can compensate for the increase in f and provide a lower energy barrier for the reaction. If there is conservation of the total bond order for a pure bond-breaking–bond-forming process, then $n^\dagger = 1$, because the average bond order for reactants and products is $n^\dagger = 2$. However, since this is not the case for the C≡N bond and the molecular species possess nonbonding electrons which can siphon electronic density into the transition state, one expects $n^\dagger > 1$. With such a transition-state bond order this reaction co-ordinate should lead to a lower energy barrier.

Table 1. Bond distensions for the reaction of HCN with bases

	Base	$\Delta G^\dagger$/kJ mol$^{-1\,a,b}$	ΔG°/kJ mol$^{-1\,b}$	d/l
1	$NCCH_2CO_2^-$	59.7	38.4	0.0757[c]
2	$ClCH_2CO_2^-$	57.8	36.0	0.0753[c]
3	$CH_3OCH_2CO_2^-$	54.1	32.2	0.0741[c]
4	$CH_3CO_2^-$	48.4	24.8	0.07235[c]
5	$H_2NC(O)NHNH_2$	48.7	29.2	0.0728[d]
6	CH_3ONH_2	44.6	24.3	0.0714[d]
7	$CF_3CH_2NH_2$	40.5	18.1	0.0709[d]
8	$ClCH_2CH_2NH_2$	30.3	1.0	0.0697[d]

[a] $\Delta G^\dagger = RT \ln (k_B T/hk)$ where k is the rate constant; T 298 K. [b] Data from ref. 4. [c] $f_r = 1.12 \times 10^4$ kJ mol^{-1} Å^{-2}, $f_p = 1.14 \times 10^4$ kJ mol^{-1} Å^{-2}, $l = 2.17$ Å. [d] $f_r = 1.12 \times 10^4$ kJ mol^{-1} Å^{-2}, $f_p = 1.13 \times 10^4$ kJ mol^{-1} Å^{-2}, $l = 2.088$ Å.

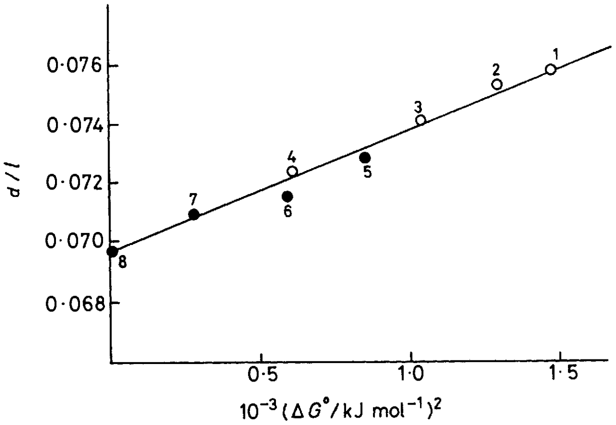
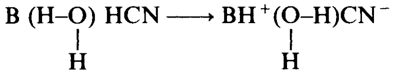


Figure 2. Plot of d/l *versus* $(\Delta G^\circ)^2$ for reactions of HCN with oxygen (●) and nitrogen (○) bases. The legend for the reactions is in Table 1

Table 1 presents the calculated d/l values together with the relevant experimental data for bond lengths and force constants.[14] According to equation (3) d/l should show a quadratic dependence on ΔG°, which is verified in Figure 2. The slope gives $\lambda = 137$ kJ mol^{-1} which is in the range of the values found for other proton-transfer reactions.[7] The intercept (0.0695) allows one to estimate $n^\dagger = 1.55$. A bond order close to 1.5 can be rationalized in terms of a molecular orbital arrangement resulting from the interaction of the lowest unoccupied molecular orbital for the nonlinear H–C≡N and one sp^x orbital of B. The counting of the electrons for the excited configuration so σ_1^2, σ_2^2, σ_3^2, σ_p^2, π_y^2, $(\pi_{nb}$ or $p_x)^1$ π_y^{*1} leads to $n^\dagger = 1.5$ for three chemical bonds. Valence structures such as $\{\bar{N}{\equiv}\dot{C}{\cdot}H{-}B \longleftrightarrow \dot{N}{\equiv}\bar{C}{\cdot}H{-}B\}^\dagger$ represent the same average transition-state bond order.

Many proton-transfer reactions of oxygen and nitrogens acids with bases are thought to proceed with participation of one or more solvent molecules.[15] The solvent molecule acts both as a



$$B\,(\underset{|}{\overset{}{H}}{-}\underset{\underset{H}{|}}{O})\,HCN \longrightarrow BH^+(\underset{\underset{H}{|}}{O}{-}H)CN^- \qquad (5)$$

proton acceptor and a proton donor. Such a mechanism can lead to a new alternative pathway if the rearrangement of the OH bonds through the solvent is a kind of Grotthuss mechanism with a synchronous and virtually activationless bond rearrangement through hydrogen bonds. The poor donor–

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‡ If the bonds vibrate in-phase the effective force constant is higher, $f = \Sigma f_i$.

Table 2. Estimated energy barriers for the reaction of HCN with HOR for the hypothetical situation of $\Delta G^\circ = 0$

Reaction co-ordinate	$f_r/10^3$ kJ mol^{-1} Å^{-2}	$f_p/10^3$ kJ mol^{-1} Å^{-2}	l/Å	d/Å	$n^\dagger$	$\Delta G^\dagger$/kJ mol^{-1}
CH and OH	3.6	4.2	2.025	0.437	0.5	92[a]
CH OH and OH OH	5.5	5.9	2.0	0.29	0.75	60
CH OH and C≡N C≡N	11.2	11.4	2.170	0.156	1.5	34.5

[a] If for mechanism 1 one takes $n^\dagger = 0.8$, identical with the value of oxygen and nitrogen acids, then $\Delta G^\dagger = 36$ kJ mol^{-1} close to the energy barrier for mechanism 3.

Table 3. Bond distensions and bond orders for proton-transfer reactions of several carbon acids

		$\Delta G^\dagger$/kJ mol^{-1}	ΔG°/kJ mol^{-1}	d/l	$n^\dagger$
	ethyl vinyl ether + H_3O^+ [a]	71.5	41.8	0.100	~1.1
1	t-butylmalononitrile + $ClCH_2CO_2^-$ [b]	85.7	58.1	0.175	
2	t-butylmalononitrile + HCO_2^- [b]	80.7	53.0	0.172	~0.72[c]
3	t-butylmalononitrile + $CH_3CO_2^-$ [b]	75.2	47.4	0.168	
4	malononitrile + HCO_2^- [b]	69.4	42.1	0.163	
5	$CH_2(CN)_2 + H_2O$ [d]	91.6	62.5	0.180	

[a] Data from ref. 1, $f_r = 7.1 \times 10^3$ kJ mol^{-1} Å^{-2}, $f_p = 6.5 \times 10^3$ kJ mol^{-1} Å^{-2}, $l = 2.356$ Å. [b] Data from ref. 17, p. 137; $f_r = 2.9 \times 10^3$ kJ mol$^-$ Å^{-2}, $f_p = 4.2 \times 10^3$ kJ mol^{-1} Å^2, $l = 2.041$ Å. [c] In the series of the dicyanocarbon acids and extrapolated at $\Delta G^\circ = 0$. [d] Data from ref. 17, p. 118; other data as in b.

acceptor properties of a current carbon acid prevents it entering into the hydrogen-bonding network of the solvent, but it is nevertheless instructive to calculate the barrier height under these ideal conditions, because HCN is a very polar molecule and can establish hydrogen bonds in water. The reactive bonds for the bond-breaking–bond-forming process are CH and BH with $n^\dagger = 0.5$. The participation of the water bridge can be considered without the formation or breaking of chemical bonds so that, for a synchronous process, $n^\dagger = 1$. The reaction co-ordinate involves both kinds of processes.

It is instructive to apply i.s.m. to estimate $\Delta G^\dagger$ for this reaction path and compare it with the one previously studied and with the direct proton-transfer process without involvement of the C≡N bond. Such a comparison is presented in Table 2 for the thermoneutral situation. The estimated energy barrier for the proton transfer through a H_2O molecule is smaller than for a normal direct proton transfer for a carbon acid, but higher than the path which involves the C≡N bond. Obviously if the rearrangement of the solvent OH bonds is not a synchronous process with the proton transfer then $n^\dagger < 1$ for H_2O,[16] and eventually the process does not compete with the first mechanism owing to the increase in the effective force constant. The calculations presented in Table 2 favour, as the mechanism for proton transfer of HCN with bases, a direct proton transfer which involves the C≡N bond along the reaction co-ordinate together with the XH bonds, but not a transfer through the solvent, in agreement with the experimental findings of Bednar and Jencks.[4]

Other Carbons Acids which approach Normal Behaviour.— The present mechanism is not exclusive of HCN. For example, proton transfer to the acetylide ion is also a fast process in the thermodynamically favourable direction.[1] Isobutylene protonation seems also to approach the normal behaviour, but since $\Delta G^\dagger$ and ΔG° differ only by 0.4 kJ mol^{-1}, less than the experimental error, it is not appropriate to apply i.s.m. to its study. A convenient system to study is the protonation of ethyl vinyl ether.[1] With the data presented in Table 3 a value of $n^\dagger \simeq 1.1$ is estimated, which is compatible, for example, with a transition-state 'structure' such as $\{>C{=}\bar{C}{\cdot}H{\cdot}B \longleftrightarrow >C{=}C{\cdot}H{\cdot}\bar{B}\}^\dagger$ or with a molecular orbital diagram of $\sigma_1^2\sigma_2^2\pi^2p_{nb}^2$, where the C=C bond is involved in the reaction co-ordinate.

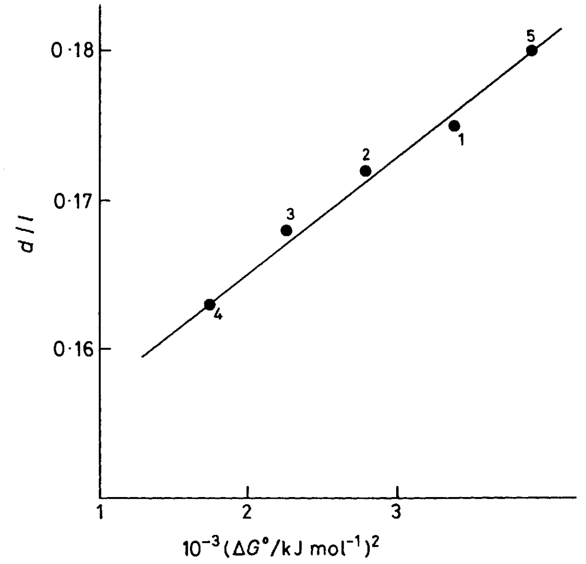

Figure 3. Plot of d/l *versus* $(\Delta G^\circ)^2$ for reactions of malononitrile and other carbon acids with bases. The legend for reactions is in Table 3

The dicyanocarbon acids approach the normal behaviour, but not as effectively as HCN or ethyl vinyl ether.[17] Since the H atom to be transferred is not linked to the carbon atom of the C≡N group, the involvement of such a group along the reaction co-ordinate is not considered. The reaction co-ordinate now involves a C–H bond in the reactants and a B–H bond in the products. The calculated data follow equation (3) well (Figure 3) with $\lambda = 100$ kJ mol^{-1} and $n^\dagger = 0.72$. The transition-state bond order is higher than the one for a typical carbon acid such as $CH_3COCH_2CO_2C_2H_5$ or CH_3NO_2 which have $n^† = 0.56$.[7] Although the cyano group is usually considered to be an effective electron-withdrawing substituent for ground-state species, it is known that its π-orbitals can have a back-donating effect. For example in the sigmatropic reactions of hexa-1,5-dienes and in the cycloaddition reactions of cyclopentadiene CN substituents are found to increase $n^†$.[16] For the present proton-transfer reactions a siphoning of *ca.* 0.3 (in two bonds) electronic charge is close to the effect observed in the sigmatropic shift reactions.

An alternative mechanism is the proton transfer through a water bridge. Since CH_3NO_2 is also a polar molecule, if such a mechanism was operating a similar behaviour would be expected for CH_3NO_2 and the malononitriles or $CH_2(CN)_2$.[17] However this is not the case, with the latter group having $n^† \simeq 0.72$ and CH_3NO_2 $n^† \simeq 0.55$. Furthermore the water-bridge mechanism for the malononitriles acids leads to a transition-state bond order ($n^† = 0.9$) incompatible with this mechanism ($n^† \leqslant 0.75$).

In conclusion the slow proton-transfer character of the typical carbon acids to bases can be attributed to the lack of electron delocalization which can increase $n^†$ and to poor hydrogen bond acceptor–donor character of carbon which prevents the transfer of protons through water in a synchronous process. The role of hybridization is not explicitly considered, because the physical features which would imply different hybrid orbitals (defined by some theoretical criterion) are the same which are revealed in changes of force constants and bond lengths.

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