

Proton transport catalysis in intramolecular rearrangements: A density functional theory study

Paola R. Campodónico^{a,*}, Juan Andrés^b, Arie Aizman^c, Renato Contreras^{d,*}

^aInstituto de Ciencias, Facultad de Medicina, Clínica Alemana Universidad del Desarrollo, código postal 771-0162, Santiago, Chile

^bDepartament de Química Física i Analítica, Universitat Jaume I, Escola Superior de Tecnologia i Ciències Experimentals, Campus del Riu Sec, 12071 Castelló de la Plana, Spain

^cDepartamento de Química, Universidad Federico Santa María, Casilla 110-V, Valparaíso, Chile

^dDepartamento de Química, Facultad de Ciencias, Universidad de Chile, Casilla 653 Santiago, Chile

A B S T R A C T

Experimental observations show that for the gas phase isomerization of protonated molecules, a third body can transport a proton from a high-energy site to a lower energy-site of the substrate, thereby catalyzing the internal rearrangement. We examine the mechanism of isomerization of isoformyl cation to formyl cation using reactivity indexes defined in the context of a conceptual density functional theory. The analysis of the group charge capacity at the transition state reveals a proton push-pull effect between the catalyst and the C=O moiety of the substrate. This effect together with the nucleofugality of the catalyst drives the proton transfer catalysis.

1. Introduction

In 1992 Bohme reported that in the proton transfer catalyzed gas phase isomerization of protonated molecules, a third body, an atom or a molecule, is able of transporting the proton from a high-energy site to a low energy-site of the protonated substrate, thereby catalyzing the internal rearrangement [1]. Experimental and theoretical works have extended the study of these catalytic processes to particles other than a proton, as for instance methyl cation, hydroxyl ion and carbenes [2–4]. Recently, Chalk and Radom reported accurate theoretical calculations of the potential energy surface for the isomerization of the isoformyl cation to the formyl cation, using a series of atomic and molecular catalysts [5]. We will rely on the structures reported by Chalk and Radom to further perform a detailed analysis of the reaction mechanism for the internal rearrangement in this system with a particular focus on the electronic properties of the transition state structure.

The catalyzed isomerization of isoformyl to formyl cations may be summarized in Scheme 1 [5]. According to this reaction scheme, three aspect may be identified as determinants of the catalyzed reaction mechanism: (i) the nucleophilicity of the catalyst X (albeit experimental and theoretical studies represent this property by the proton affinity (PA) or the gas phase basicity); (ii) the charge capacity of the X and C=O moieties at the transition state struc-

tures (TS) that creates a proton push-pull effect and (iii) the leaving group ability of the catalyst (i.e. its nucleofugality) at the TS stage of the rearrangement. In this work we use the concepts of nucleophilicity [6–11], charge capacity [12], and nucleofugality [13–17], in order to rationalize the proposed proton transfer catalyzed mechanism.

2. Model equations and computational details

2.1. The nucleophilicity index

The definition of a nucleophilicity index is still an open problem. The difficulty to define a nucleophilicity number, within a similar framework to that leading to the definition of electrophilicity has a rather simple explanation: a thermodynamically stable (nucleophilic or electrophilic) species must have a negative value of the electronic chemical potential μ . This means:

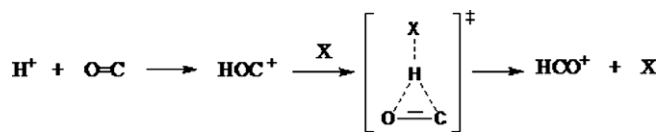
$$\mu = \left[\frac{\partial E}{\partial N} \right]_{v(r)} \cong \left[\frac{\Delta E}{\Delta N} \right]_{v(r)} < 0 \quad (1)$$

For electrophilic species one has $\Delta N > 0$ and $\Delta E < 0$, so that the second order energy expression for $E_v[N]$ has a minimum for a given $N + \Delta N_{\max}$ value at constant external potential $v(r)$ [12]. Using a simple variational calculation, Parr et al. [12] defined the electrophilicity index ω as follows:

$$\omega = \frac{\mu^2}{2\eta} \quad (2)$$

* Corresponding authors. Fax: +56 2 2713888 (P.R. Campodónico); +56 2 2999306 (R. Contreras).

E-mail addresses: pcampodonic@udd.cl (P.R. Campodónico), rcontrer@uchile.cl (R. Contreras).



Scheme 1. Reaction path for the intramolecular proton transport catalysis.

The maximum additional electronic charge, ΔN_{\max} that an electrophilic species may accept from the environment is given by:

$$\Delta N_{\max} = -\frac{\mu}{\eta} = -\mu S \quad (3)$$

where η is the chemical hardness of the system, which acts a resistance to the exchange of electronic charge with the environment; and $S = 1/\eta$ is the chemical softness. However, for nucleophilic species, condition Eq. (1) entails that for $\Delta N < 0$ the energy change must be always positive, and the function $E_v[N]$ is this time not convex, and therefore the function $E_v[N]$ has no minimum in a finite interval ΔN . Now the question is: among a family of related compounds which is the best nucleophile? Under the constraint that $\Delta E > 0$, a reasonable answer is the following: the best nucleophile will be that species that after releasing a fraction of electronic charge to the environment is the less destabilized in energy. This means that, mathematically, one should minimize the lost of stability, a variational calculation which is apparently harder to perform than the one leading to the definition of electrophilicity. Variational techniques applied in conditions of inequalities are often found in mathematical economics, such as the Kuhn–Tucker theorem [18]. There is however a simpler answer based on chemical intuition: if we place the problem in the limit case in which exactly one electron unit is transferred to the environment, the criterion of the less destabilized species leads to the following empirical definition of nucleophilicity ω^- [6]:

$$\omega^- = -I \approx \varepsilon_{\text{H}} \quad (4)$$

where I is the first vertical ionization potential, and ε_{H} is the one electron energy of the HOMO orbital. In defining a nucleophilicity index by Eq. (4), Koopman's theorem has been used. The relationship between nucleophilicity and ionization potential in solution phase has been already shown by us to hold for experimental I and ω^- values [6]. In this work, we shall use Eq. (4) as a model definition for the intrinsic nucleophilicity in the gas phase.

2.2. The charge capacity index: Proton push–pull effect at the transition state

Still with reference to Scheme 1, there are two additional features that may contribute to the proton transfer catalysis. At the transition state, there is the effect of the proton affinity of the moieties C=O and X which will determine the direction of the proton migration. There are conceptual DFT approach that address the PA directly [19,8]. Unfortunately, proton affinity is a global property of a molecule and therefore it is not possible to estimate the PA of a fragment within a complex like the TS structure. In fact, Chalk and Radom [5] reported that one of the factors playing a role in the proton catalysis is the difference in proton affinity between the isolated catalyst X and the C=O fragment: $\delta\text{PA} = \text{PA}(\text{X}) - \text{PA}(\text{C}=\text{O})$. Proton transfer has been shown to display a tight correlation with the electronic chemical potential [20]. This relationship is based on Scheine's observation [21] that within a H-bonded complex $[\text{A}\cdots\text{H}\cdots\text{B}]^+$ if $\text{PA}(\text{A}) > \text{PA}(\text{B})$ then the proton will spontaneously migrate from B to A, and that at the same time, the compensating charge transfer will take place in the opposite direction. Scheine's observation is suitable for the purpose of indirectly modelling a 'group proton affinity' in the form of a proton

push–pull effect which is framed on the charge capacity concept defined in Eq. (2) as follows: we start by rewriting Eq. (2) using the additive property of chemical softness, namely:

$$\begin{aligned} \Delta N_{\max} &= -\frac{\mu}{\eta} - \mu S = -\mu \sum_k s_k^+ - \mu \sum_k f_k^+ S = \sum_k \Delta N_{\max} f_k^+ \\ &= \sum_k \Delta N_{\max}(k) \end{aligned} \quad (5)$$

The condensed to atom k charge capacity is then given by:

$$\Delta N_{\max}(k) = \Delta N_{\max} f_k^+ \quad (6)$$

where f_k^+ is the electrophilic Fukui function. The group or fragment charge capacity $\Delta N_{\max}(\text{G})$ is simply obtained from:

$$\Delta N_{\max}(\text{G}) = \sum_{k \in \text{G}} \Delta N_{\max}(k) \quad (7)$$

for $\text{G}=\text{X}$, $\text{C}=\text{O}$.

2.3. The nucleofugality of the catalyst at the transition state

The second additional feature contributing to the proton catalysis at the transition state concerns the leaving group ability (i.e. nucleofugality) of the catalyst. Nucleofugality indexes have been proposed by Ayers [13] and by us to model the leaving group ability of nucleofuges in nucleophilic substitution and elimination reactions [14–16]. Even though Ayer's nucleofugality ν scale is more universal than the one proposed by us earlier, we will use the permanent group (PG) dependent group electrophilicity based scale $\nu(\text{PG})$ only for the sake of consistency. Nucleofugality may be quantitatively represented by the following expression [13–16]:

$$\nu(\text{PG}) = \omega_{\text{G}} = \sum_{k \in \text{G}} \omega_k \quad (8)$$

where $\omega_k = f_k^+ \omega$, is the regional electrophilicity condensed to atom k [14].

As stated in Section 1, we used the optimized structures reported by Chalk and Radom [5] at G2 level of theory, to perform HF/6-311G (d,p) single point calculations to obtain the electronic properties needed to compute the DFT reactivity indexes using the GAUSSIAN 98 suite of programs [22]. The condensed to atom electrophilic and nucleophilic Fukui functions were obtained from a method described elsewhere [23].

3. Results and discussion

A general requisite is that any proton catalyst must display a significant proton affinity (PA) to bind a proton prior to the electrophilic attack to the substrate (C=O in the present case). Up to now there is no clear relationship between PA and nucleophilicity. For instance, the spectroscopic nucleophilicity scale reported by Legon and Millen suggests that the intermolecular force constant between nucleophiles B and a HX (X = F, Cl, I) probe in the H-bonded X–H...B complex provides a limit gas phase nucleophilicity of B [24]. This result shows that the strength of H-bond, PA and intrinsic (gas phase) nucleophilicity are related concepts. In the present study we have found that there exist a significant correlation between the experimental PA and the nucleophilicity index defined in terms of the HOMO energy. This comparison is shown in Fig. 1. It may be seen that the series of potential catalysts X quoted in Table 1, split out into three subseries including the inert gases (He, Ne, Ar, Kr), the isoelectronic (10 electrons) σ donors (HF, H₂O, CH₄, and NH₃) series and the isoelectronic (14 electrons) π donors (N₂, CO, HCN) series. Therefore, it seems that the nucleophilicity index defined in Eq. (4) correlates fairly well with the experimental PA [5,25] within an isoelectronic series. A fourth series of

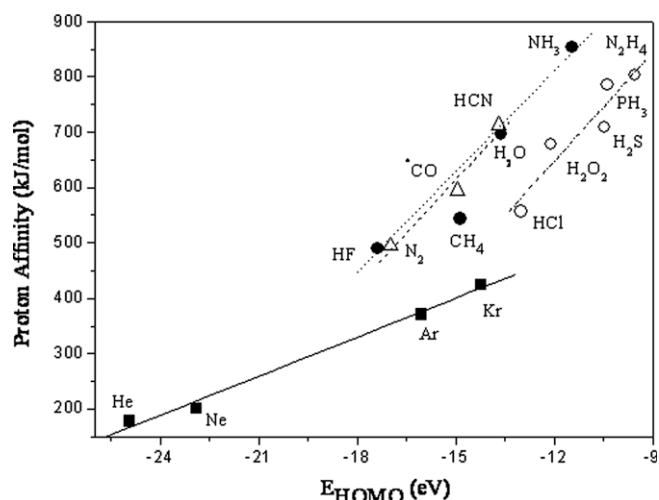


Fig. 1. Comparison between experimental proton affinities and the one electron energy of the HOMO.

isoelectronic (18 electrons) nucleophiles (HCl, H₂O₂, H₂S, PH₃, N₂H₄) was selected to test this relationship. The comparison between PA of this series and the proposed nucleophilicity index is also included in Fig. 1. It may be seen that the trend is conserved.

Table 1 also quotes the local nucleophilicity as an indicator of site selectivity towards a proton. This index is relevant for the case of poly-functional systems presenting more than one site of protonation. The most important case is that of CO. Using the nucleophilic Fukui function, it may be seen that the protonation site of CO is the carbon atom (which was denoted by *CO in Ref. [5]). Another relevant case is that of CN⁻. Note that in this case, the selectivity towards protonation is almost symmetrically distributed over the C and N centers. All the remaining cases are trivial because they show an unique or equivalent sites of protonation.

However, it is the PA difference rather than the absolute value of PA which is relevant for proton catalysis. This is because a high PA value for the catalyst may cause the proton transfer reaction to compete with the proton transport catalytic process [5]. In other words, there is a finite range of PA's for which the catalytic effect is operative. This range is determined by the difference $\delta\text{PA} = \text{PA}(\text{X}) - \text{PA}(\text{substrate})$. According to Scheme 1, this difference must be settled at the transition state of the isomerization process. This is because, according to Chalk and Radom, the interaction energy of X at the transition state, reactants and products followed the order: $\text{X} \cdot \text{TS} > \text{X} \cdot \text{HOC}^+ > \text{X} \cdot \text{HCO}^+$ [5]. However, and as stated in Section 2.2, proton affinity is a global property of a molecule and therefore it is not possible to estimate the PA of a fragment within a complex like the TS structure. A useful relationship that may help to find an answer for this problem is the one previously found between PA's and the electronic chemical potential [8]. From this relationship, the model described in Section 2.2 may be applied. Specifically, the group charge capacity defined in Eq. (7) probes the proton motion as taking place in the opposite direction of charge transfer. Values of $\Delta N_{\text{max}}(\text{G})$ for fragments X and CO are quoted in Table 2. It may be seen that for the series of inert gases for which proton transfer catalysis has been evaluated, while the group charge capacity at X increases the group charge capacity of C=O decreases from 0.68 e in He to 0.20 e in Ar, thereby suggesting that in going from He to Ar, the proton is in some way pulled from X to the C=O moiety of the substrate. The proton pull effect towards the C=O moiety of the cation at the transition state follows the order He < Ne < Ar; a result which is in qualitative agreement with the computed energy barriers for the proton-catalyzed isomerizations. Following Chalk and

Table 1

One electron orbital energies, nucleophilicity index (ν^-), nucleophilic Fukui function, local nucleophilicity (ω_k^-) and experimental proton affinities for inert gases and some selected σ and π electron donors

	E_{HOMO} (eV)	E_{LUMO} (eV)	ν^- (eV)	Atom/sites	f_k^-	ω_k^-	PA ^a (kJ/mol)
He	-24.95	22.57	-24.95	He	1.00	-24.95	178
Ne	-22.90	20.41	-22.90	Ne	1.00	-22.90	201
Ar	-16.06	13.57	-16.06	Ar	1.00	-16.06	371
Kr	-14.25	11.56	-14.25	Kr	1.00	-14.25	424.6
HF	-17.39	4.10	-17.39	F	0.99	-17.22	489.5
				H	0.01	-	
H ₂ O	-13.62	4.15	-13.62	O	0.98	-13.35	697
				H	0.01	-	
				H	0.01	-	
NH ₃	-11.46	4.30	-11.46	N	0.94	-10.77	854
				H	0.02	-	
				H	0.02	-	
				H	0.02	-	
CH ₄	-14.86	4.42	-14.86	C	0.53	-7.88	543.5
				H	0.07	-	
				H	0.16	-	
				H	0.12	-	
				H	0.12	-	
C=O	-14.96	4.27	-14.96	C	0.95	-14.21	594
				O	0.05	-	
N ₂	-16.99	4.91	-16.99	N	0.50	-8.50	494.5
				N	0.50	-	
HCN	-13.70	4.14	-13.70	N	0.53	-7.26	712
				C	0.47	-6.44	
				H	0.00	-	
H ₂ O ₂	-12.09	4.43	-12.09	O	0.49	-5.92	678
				O	0.49	-5.92	
				H	0.01	-	
				H	0.01	-	
H ₂ S	-10.47	3.57	-10.47	S	1.00	-10.47	709
				H	0.00	-	
				H	0.00	-	
HCl	-13.02	3.37	-13.02	Cl	0.99	-12.89	557
				H	0.01	-	
PH ₃	-10.39	3.72	-10.39	P	0.88	-9.14	786.6
				H	0.04	-	
				H	0.04	-	
				H	0.04	-	
N ₂ H ₄	-9.55	4.41	-9.55	N	0.48	-4.58	803
				N	0.48	-4.58	
				H	0.01	-	
				H	0.01	-	
				H	0.01	-	
				H	0.01	-	

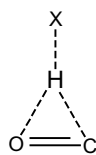
^a All experimental values were taken from Refs. [5,8].

Radom's explanation, the marginal catalytic effect promoted by He is related to a weakening of the O-H bond that facilitates the proton migration from the O to the C ends of C=O. Note that within the present model, the weakening of the O-H bond may be viewed as a pull effect of the proton towards He, in view of its vanishing charge capacity at the transition state. For the remaining inert gases, this effect becomes more balanced, thereby facilitating the proton migration between the O and C centers of the C=O fragment at the TS structure. The net effect is a further lowering of the energy barrier.

The presence of HF, N₂, and *CO as proton transport catalysts promote similar and enhanced effects. The *CO species is being considered instead of CO* to be consistent with the proton selectivity predicted from the results quoted in Table 1, based on the values of the nucleophilic Fukui function. For this subseries, Chalk and Radom predicted negative barriers for the catalyzed isomerization. Following these authors, N₂ and HF present PA's that lie between those of CO* and *CO, and therefore they become conveniently placed to drag a proton from HOC⁺ to X and then to re-deposit it at the carbon center to yield the isomer HCO⁺ (see Scheme 1) [5].

Table 2

Electronic parameters, electrophilic Fukui function, charge capacity, nucleofugality indexes transfer, and theoretical isomerization barriers



X	μ (eV)	η (eV)	S (eV)	ω (eV)	Atom/sites	f_k^+	ΔN_{\max} (e unit)	$\Delta N_{\max} X$ (e unit)	$\Delta N_{\max} H$ (e unit)	$\Delta N_{\max} CO$ (e unit)	$v(\text{PG})^-(X)$ (eV)	Barrier ^a (kJ mol ⁻¹)
He	-15.77	17.05	0.06	7.29	He	0.00	0.93	0.00	0.25	0.68	0.00	138
					H	0.27						
					O	0.35						
					C	0.38						
Ne	-15.02	17.29	0.06	6.53	Ne	0.01	0.87	0.01	0.20	0.57	0.06	131
					H	0.23						
					O	0.32						
					C	0.44						
Ar	-12.49	16.71	0.06	4.66	Ar	0.09	0.75	0.07	0.49	0.20	0.42	33
					H	0.65						
					O	0.10						
					C	0.16						
HF	-12.65	16.54	0.06	4.84	H	0.69	0.77	0.53	0.13	0.11	3.34	-69
					F	0.00						
					H	0.17						
					O	0.04						
N ₂	-12.71	15.02	0.07	5.38	C	0.10	0.85	0.82	0.01	0.02	5.22	-69
					N	0.40						
					N	0.57						
					H	0.01						
O=C ⁺	-12.61	14.38	0.07	5.53	O	0.24	0.88	0.86	0.01	0.01	5.42	-163
					C ⁺	0.74						
					H	0.01						
					O	0.00						
O=C	-12.56	15.99	0.06	4.93	C	0.01	0.79	0.77	0.01	0.01	4.83	-10
					O ⁺	0.12						
					H	0.01						
					O	0.12						
H ₂ O	-11.69	16.23	0.06	4.21	C	0.86	0.72	0.58	0.10	0.04	3.41	-258
					H	0.43						
					H	0.38						
					O	0.00						
NH ₃	-10.96	16.45	0.06	3.66	H	0.14	0.67	0.54	0.10	0.03	2.96	-419
					H	0.01						
					C	0.04						
					H	0.27						
NH ₃	-10.96	16.45	0.06	3.66	H	0.27	0.67	0.54	0.10	0.03	2.96	-419
					H	0.27						
					H	0.27						
					N	0.00						
					H	0.15						
					O	0.01						
					C	0.03						

^a Theoretical isomerization energy barriers evaluated at G2 level of theory taken from Ref. [5].

Note that group charge capacity of HF and N₂ appears consistently upper bounded by those of OC* ($\Delta N_{\max}(\text{OC}^*) = 0.86$ e, see Table 2). However the presence of the neutral catalysts H₂O and NH₃ break the regime where the proton transfer catalysis is operative. In these cases a strong decrease in the group charge capacities below the $\Delta N_{\max}(\text{OC}^*) = 0.86$ e threshold is observed, thereby suggesting that the proton is likely to be bound by the X moiety to yield the intermolecular proton transfer products H₃O⁺ + CO and NH₄⁺ + CO, respectively. Note that for X = H₂O and NH₃, the charge capacity at the proton has fallen to 0.10 e, thereby suggesting that at the transition state, some coordinated covalent bonding to H₂O and NH₃ is being formed. This result is also in close agreement with the highly accurate energy calculations reported by Chalk and Radom [5].

A final remark involves the leaving group ability of the catalyst X at the TS structures. We must however consider three different

regimes: the first one is that of a weak interaction between the catalyst X and the TS structures for inert gases. For He and Ne, for which a marginal relative decrease in energy barrier is observed, the nucleofugality pattern is consistently predicted as marginal. Note however that in passing from (He, Ne) to Ar, a significant increase in the leaving group ability of the catalyst is observed. This effect works in the direction of an effective catalysis. For the second subseries of moderate interaction energy between X and the TS structures (i.e. for X = HF, N₂, and O=C*), the leaving group ability significantly increases from 3.34 eV in HF to 5.42 eV in O=C*. Note that for this subseries, which was reported to contain the optimum proton transport catalysts, both the proton push-pull effects and the nucleofugality of the catalyst cooperatively contribute to an effective catalytic effect. For the third subseries showing a strong interaction between the catalyst X and the TS structures that includes the catalysts H₂O and NH₃, the

nucleofugality pattern is predicted to fall from the maximum nucleofugality value of 5.42 eV in O=C* to the values 3.41 eV and 2.96 eV for H₂O and NH₃ respectively, thereby showing an effect that works in the opposite direction of the proton transfer catalysis. This last result may be understood as follows: from Chalk and Radom calculations, in the case of water, the intermolecular proton transfer products H₃O⁺ + C=O are 94.0 kJ/mol below the HCO⁺ + H₂O isomerization product. For NH₃ this difference is enhanced to 260 kJ/mol in favor of the intermolecular proton transfer products NH₄⁺ + HCO⁺. These results are coherent with our model if the nucleofugality values for H₃O⁺ and NH₄⁺ are greater than those of H₂O and NH₃, respectively. Using the values quoted in Table 2, it may be found that $\nu(\text{PG})^-(\text{H}_3\text{O}^+)$ (4.0 eV) > $\nu(\text{PG})^-(\text{H}_2\text{O})$ (3.41 eV) and that $\nu(\text{PG})^-(\text{NH}_4^+)$ (3.51 eV) > $\nu(\text{PG})^-(\text{NH}_3)$ (2.96 eV). These results confirm the prediction that in the regime of a strong X-TS interaction, the intermolecular proton transfer process outweighs the proton transfer catalysis.

4. Concluding remarks

The catalytic effect promoted by a third body on the isomerization of isoformyl to formyl cations has been discussed in detail using reactivity indexes defined in the context of the conceptual density functional theory, and a simple model of nucleophilicity. We have found that among the three factors that may contribute to the intramolecular catalytic process, the difference in group charge capacity between the catalyst and the C=O moiety of the substrate causes a proton push-pull effect at the transition state that correctly explains the variation of the energy barriers for the isomerization reaction. The nucleofugality of the leaving catalyst at the TS stage also works in the direction of favoring the catalytic process in the weak and moderate interaction regimes. In the limit of a strong X-TS interaction regime, the intermolecular proton transfer process is predicted to be the preferred channel.

Acknowledgements

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