

## Letter

Hydrogen bonding and dissociation effects  
on the gas phase proton transfer reactions of ozoneR. Contreras<sup>1,2\*</sup>, V. S. Safont<sup>1</sup>, J. Andrés<sup>1</sup>, P. Pérez<sup>1,2\*</sup>, A. Aizman<sup>3</sup>, O. Tapia<sup>2</sup><sup>1</sup> Department de Ciències Experimentals, Universitat Jaume I, Box 242, E-12080 Castelló, Spain<sup>2</sup> Department of Physical Chemistry, Uppsala University, Box 532, S-75121 Uppsala, Sweden<sup>3</sup> Departamento de Química, Universidad Técnica F. Santa María, Casilla 110-V, Valparaíso, Chile

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**Abstract.** Recently, the proton affinity (PA) of ozone was experimentally determined by Cacace and Speranza [Science (1994) 265: 208] using a bracketing technique that involved the proton transfer (PT) reactions:  $O_3H^+ + B \rightleftharpoons O_3 + BH^+$ ; for different Brønsted bases B. These authors showed that the simple collision model is not adequate to describe PT. We now present a theoretical model reflecting this bracketing procedure by explicitly introducing H-bonding complexing, dissociation and PT contributions, to discuss the kinetic model that assumes that PT occurs through one elementary step. The methods used include semiempirical density functional theory and ab initio Hartree-Fock methods. The procedure is gauged by using estimated PA of ozone obtained from deprotonation reactions including the Brønsted bases  $B=NH_3$ ,  $H_2O$ ,  $HOCl$ ,  $SO_2$ ,  $CH_3F$  and Kr. The PA-obtained range was from 145.3 to 160.3 kcal/mol, in fair agreement with the experimental value of  $148.0 \pm 3$  kcal/mol. The model seems to be fairly independent of the reference bases used to evaluate the PA. H-bonding effects appear to be a determining factor to explain collision efficiencies.

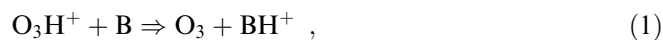
**Key words:** Gas phase proton transfer reactions – H-bonding effects – Dissociation effects

## 1 Introduction

The gas phase chemistry of ozone has received a great deal of attention due to its obvious impact on the environmental sciences. Concern is mainly focused on the problem of the depletion of the stratospheric ozone [1–3]. Due to its unshared electron pairs, ozone is expected to behave as a nucleophile, but it may also

react as an electrophilic agent [4, 5]. The Brønsted-base character of  $O_3$  involves the protonated form  $O_3H^+$ , which was introduced by Olah [5, 6] to explain the ozonolysis of alkanes. The gas phase equilibrium between  $O_3$  and  $O_3H^+$  is exclusively described by the proton affinity (PA) of ozone.

Recently, the PA of ozone has been experimentally obtained from mass spectrometric experiments that used a Fourier transform ion cyclotron resonance (ICR) technique [4]. The authors proposed a method using reference Brønsted bases B involved in the proton transfer (PT) reaction:



where B is a base of adequate strength.

PAs, as single numbers, can be correlated with kinetic data if the PT reactions occur at, or very close to, the collision rate [7]. In this case, this is equivalent to assuming that PT takes place through an elementary step. However, recent experimental results obtained from ICR have jeopardized this kinetic model because they showed the relevance of H-bonding [8–10] and dissociation effects on PT reactions. One way or another, the PT process takes place in collision complexes having lifetimes larger than those required for simple transfer.

The PAs are usually obtained as a *single number*, by comparing the total energies of the neutral and protonated forms. The PA of ozone was predicted using different and highly sophisticated computational techniques [11–13]. The best calculation was that of Meredith et al. [13], who reported a value of 149.5 kcal/mol at 298 K.

In this work, we present a model of PT that explicitly introduces H-bonding and dissociation contributions to PT reactions and uses the empirical PAs of the bases to close the thermodynamic cycle. The quality of this procedure, applied to the deprotonation reaction (1), can be gauged from the fairly accurate values of ozone PA obtained. They are independent of the Brønsted base used as a reference. The model is appropriate to explain the observed collision efficiency curves obtained in gas

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phase PT experiments since H-bonding would increase the lifetime of the collision complexes, as will be discussed below.

## 2 Model and calculations

The gas phase PT process (1) may be decomposed into H-bonding ( $\Delta H_{\text{hb}}$ ) and dissociation ( $\Delta H_d$ ) contributions [14] as shown in Fig. 1.

The PT energy variations,  $\Delta H_{\text{pt}}$ , can be related to the PA of ozone,  $\text{PA}(\text{O}_3)$ , by:

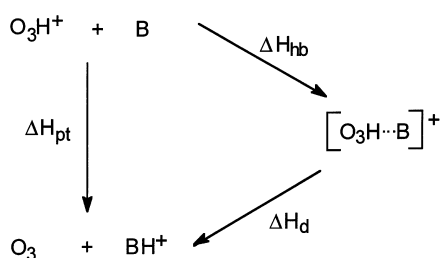
$$\text{PA}(\text{O}_3) = \text{PA}(\text{B}) + \Delta H_{\text{pt}} = \text{PA}(\text{B}) + \Delta H_{\text{hb}} + \Delta H_d, \quad (2)$$

where  $\text{PA}(\text{B})$  is the PA of the base used as a reference. In this report we used the series  $\text{B}=\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{HOCl}$ ,  $\text{SO}_2$ ,  $\text{CH}_3\text{F}$  and  $\text{Kr}$ . The estimates of  $\text{PA}(\text{O}_3)$  reported here use the theoretically calculated hydrogen bond and dissociation energy terms with empirical  $\text{PA}(\text{B})$ . The quantity  $\Delta H_{\text{hb}}$  was obtained by taking the enthalpy difference between the H-bonded complex  $[\text{B}-\text{HO}_3]^+$ , and the separated species  $\text{B}$  and  $\text{O}_3\text{H}^+$ . The dissociation contribution  $\Delta H_d$  involves the enthalpy variation between the  $[\text{B}-\text{HO}_3]^+$  complex and the separated species  $\text{BH}^+$  and  $\text{O}_3$ . The entropic terms have been neglected, thus estimating the PA of ozone as an enthalpy.

The calculations were performed based on density functional theory (DFT), using the Amsterdam Density Functional (ADF) package [15], and at the ab initio Hartree Fock (HF) level using the GAUSSIAN94 package [16]. The DFT approach was made at the BP/86 level, in which the Kohn-Sham self-consistent equations [17] are solved, using the local density approximation of Vosko [18], with gradient corrections for exchange as suggested by Becke [19] and the non-local gradient correction for correlation proposed by Perdew [20]. A triple-zeta with two polarization function basis sets was used. The ab initio calculations were made at the restricted HF/6-31++G\*\* [21] level. Full geometry optimization was performed in all species involved in the three steps of the thermodynamic cycle shown in Fig. 1. The Berny analytical gradient routines [22] were used for optimization in the HF calculations, while for DFT calculations the Murtagh-Sargent method was employed [23].

## 3 Results and discussion

Table 1 shows the predicted values for  $\text{PA}(\text{O}_3)$  obtained from Eq. (2) for the series, using the experimental values



**Fig. 1.** Thermodynamic cycle for the partitioning of proton transfer energies ( $\Delta H_{\text{pt}}$ ) into H-bonding ( $\Delta H_{\text{hb}}$ ) and dissociation ( $\Delta H_d$ ) contributions

**Table 1.** Predicted proton affinity (PA) of ozone using different reference bases<sup>a, b</sup>

B	Method	$\text{PA}(\text{O}_3) =$	$\text{PA}(\text{B})^c +$	$\Delta H_{\text{pt}}$
NH <sub>3</sub>	ADF	149.5	203.5	-54.0
	HF	149.8		-53.7
H <sub>2</sub> O	ADF	152.7	166.7	-14.0
	HF	152.3		-14.4
HOCl	ADF	151.1	153.1 <sup>d</sup>	-2.0
	HF	151.2		-1.9
SO <sub>2</sub>	ADF	145.3	150.9	-5.7
	HF	146.7		-4.2
CH <sub>3</sub> F	ADF	157.5	145.0	12.5
	HF	149.8		4.8
Kr	ADF	151.7	101.6	50.1
	HF	160.3		58.7

<sup>a</sup> All energy values in kcal/mol

<sup>b</sup> HF refers to HF/6-31++G\*\*. Energy values are given at standard temperature; thus the zero point energy corrections and temperature corrections have been taken into account

<sup>c</sup> Experimental values of  $\text{PA}(\text{B})$  from references [4, 24–27]

<sup>d</sup> In the absence of an experimental value for  $\text{PA}(\text{HOCl})$ , the predicted value of Ref. [24] was used

of  $\text{PA}(\text{B})$ , except for the case of  $\text{HOCl}$ , for which the experimental value is unavailable. For this system we used the theoretical value reported by Francisco and Sander [24]. It may be seen that the PA values range from 145.3 (ADF) to 160.3 (HF) kcal/mol. It is worth noticing that ADF (with the exception of  $\text{CH}_3\text{F}$ ) and HF/6-31++G\*\* (with the exception of  $\text{Kr}$ ) predict PA values in fair agreement with the experimental value of  $148.0 \pm 3.0$  kcal/mol reported in Ref. [4], and also in good agreement with the theoretical value reported by Meredith et al. [13], from very elaborate ab initio calculations.

It is worth emphasizing that Eq. (2) provides a model for the PA of ozone that is almost independent of the reference base used. This independence requires that the PT contribution is highly correlated with the PA of the base used as a reference (see Table 2): with the exception of  $\text{SO}_2$ , the PT energies follow the reverse order

**Table 2.** Proton transfer energy decomposition into H-bonding and dissociation contributions<sup>a, b</sup>

B	Method	$\Delta H_{\text{pt}}$	$\Delta H_{\text{hb}}$	$\Delta H_d$
NH <sub>3</sub>	ADF	-54.0	-62.0	8.0
	HF	-53.7	-60.2	6.5
H <sub>2</sub> O	ADF	-14.0	-35.9	21.9
	HF	-14.4	-28.9	14.5
HOCl	ADF	-2.0	-25.2	23.2
	HF	-1.9	-17.8	15.9
SO <sub>2</sub>	ADF	-5.7	-10.5	4.8
	HF	-4.2	-21.0	16.9
CH <sub>3</sub> F	ADF	12.5	-16.7	29.2
	HF	4.8	-21.3	26.1
Kr	ADF	50.1	-7.5	57.6
	HF	58.7	-3.3	62.0

<sup>a</sup> Energy variations in kcal/mol

<sup>b</sup> HF refers to HF/6-31++G\*\*. Energy values are given at standard temperature; thus the zero point energy corrections and temperature corrections have been taken into account

displayed by the gas phase basicity, approached by the PAs of the bases [25], measured in kcal/mol: Kr, PA = 101.6 [4]; CH<sub>3</sub>F, PA = 145.0 [4]; SO<sub>2</sub>, PA = 150.9 [4]; HOCl, PA = 153.1 [24]; H<sub>2</sub>O, PA = 166.7 [26]; and NH<sub>3</sub>, PA = 203.5 [27].

The predicted order of H-bonding strength, in absolute value, NH<sub>3</sub> > H<sub>2</sub>O > HOCl > CH<sub>3</sub>F > SO<sub>2</sub> > Kr, obtained from ADF calculations, follows the trend of the PAs of the reference bases. HF results show a different position of HOCl within this order (NH<sub>3</sub> > H<sub>2</sub>O > CH<sub>3</sub>F > SO<sub>2</sub> > HOCl > Kr). According to the results shown in Table 2, the H-bonding contribution drives the PT process for B=NH<sub>3</sub>, H<sub>2</sub>O and SO<sub>2</sub>. For B=HOCl, the H-bonding and dissociation contributions compensate for each other. For CH<sub>3</sub>F and Kr, the dissociation contribution drives the PT reaction, which is predicted to be thermodynamically unfavourable. This result is in agreement with the experimental data for collision efficiency of Cacace and Speranza [4]: Kr was found to display the lowest PT probability within the series.

If the PT occurs as predicted by the kinetic model (i.e. through an elementary step), then there is a probability near to 1 of populating the states of the outgoing channel. This might be true for highly exothermic steps. If the PT reaction occurs according to our assumed model depicted in Fig. 1, two limiting cases can be found:

1. The dissociation energy is larger than the hydrogen bond. Here, the interconversion will be affected by H-bonding, but it will also depend upon the energy barrier for relative kinetic energy about and above threshold.
2. The reaction is mildly exothermic. Here, the interconversion would be affected by H-bonding again.

The role of H-bonding effects on PT reactions may be also discussed within an electronic quantum model of chemical reactions [28]. A chemical reaction may be considered to correspond to a change of electronic quantum states from reagents to products. At the bottleneck (represented here by quantum states sustained by the saddle point of index one or transition structure) the classical potential curve associated with the proton transfer process is too crude a model. The reason is rooted in general quantum mechanics: it is not possible to qualitatively change two different electronic states with an adiabatic process (such an idea is possible only in the Born-Oppenheimer adiabatic scheme). The proton transfer can be seen as a change in quantum electronic state characteristic of an activated precursor complex for the ingoing channel,  $\Psi_{\text{in}}(\text{O}_3^+ \cdots \text{HB})$  into an activated successor complex  $\Psi_{\text{out}}(\text{O}_3 \text{H} \cdots \text{B}^+)$  for the outgoing channel. The geometric fluctuations must then overlap those defining the bottleneck for PT. The changes take place as a Franck-Condon (fixed nuclei) process at the bottleneck region. From a semiclassical point of view, the reagents have finite relative kinetic energies and the ro-vibrational states of the H-bonded complex may be assessed by the collision complex. The interaction between the H-donor and H-acceptor partners may increase the lifetime of the collision complexes, thereby increasing the probability of populating the quantum

states of outgoing channel system. In other words, an increase in the density of states of the collision complex at the bottleneck produces an increased lifetime, so that the probability of populating  $\Psi_{\text{out}}(\text{O}_3 \text{H} \cdots \text{B}^+)$  augments, and with it, the collision efficiency in the global PT process. Our results in Table 2 show that the stronger the stabilization of the H-bonded complex, the greater is the efficiency of the PT reaction. This conclusion seems to be confirmed by the experimental data reported by Cacace and Speranza [4].

Furthermore, the results shown in Table 1 are also in agreement with the collision efficiency of the PT reaction (1): Kr displays the lowest collision efficiency and water displays the highest within the series used in Ref. [4]. Comparison with NH<sub>3</sub> is not possible because this base was not included in the experimental data of Cacace and Speranza. However, from Eq. (2) we predict that NH<sub>3</sub> should display an even higher collision efficiency in the deprotonation process (1). On the other hand, the availability of reliable theoretical PT energies is stimulating because they may be used in connection with transition state theory to yield more quantitative representations of the PT rate constants, thereby allowing the calculation of PT probabilities. An additional requirement to be fulfilled is the accurate calculation of the potential energy surfaces.

#### 4 Concluding remarks

The gas phase PT reactions of ozone with a series of Brønsted bases have been examined in terms of H-bonding and dissociation contributions. H-bonding effects seem to play a determining role for the collision efficiency of PT. Our results, interpreted within the quantum model of chemical interconversion [28], suggest that the (ro-vibrational) excited states of the bound H-bonded species may be considered as mediating the interconversion into PT products, in the sense of increasing the lifetimes of collision complexes at the bottleneck region [29]. Within this model, the lower the local minimum associated with the H-bonded activated complexes, the greater is the number of quantum states available for effective collisions. This conclusion is in agreement with the correlation found here between H-bonding energy and the experimental collision efficiency data.

On the other hand, despite the diversity of the electronic structure of the reference bases used in our thermodynamic cycle, the proposed model yields accurate values for the PA of ozone and these are almost independent of the proton acceptors. It is also worth mentioning that, in general, the model appears to be almost independent of the methodology used to evaluate the energy changes involved in the thermodynamic cycle: semiempirical DFT calculations quantitatively reproduce the PA of ozone from PT reactions, involving quite different chemical environments, and therefore they may be a good alternative to more elaborate ab initio techniques. Finally, the present model yields reliable estimates of PT energies which may be useful in the analysis of collision efficiencies in gas phase PT experiments.

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