Concerning the Basicity of Ozone

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A comprehensive view on the basicity order of simple molecules, including ozone, is reported and contrasted with recent estimates in heterogeneous systems.[1]

In a recent paper Mariey, Lamotte, Hoggan, Lavalley, Boulanine, and Tsyganenko (MLHLBT) report the results of a IR spectroscopic study aimed at estimating the basicity of O_3.[1] Apparently, the authors have overlooked previous theoretical and experimental studies specifically devoted to the quantitative evaluation of the basicity of O_3, through the measurement of its gas-phase proton affinity (PA), and the determination of the structure and the reactivity of its conjugated acid HO_3^+. In order to give a more balanced view of the problem, a brief outline of pertinent theoretical and experimental results, and their comparison with the salient conclusions reached by MLHLBT seem in order.

There exist experimental studies[2,3] on gaseous HO_3^+, performed by Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry (FTICR-MS), whose results lead to a $PA(O_3)=148\pm3$ kcal mol^{-1}. From a theoretical point of view, the protonation of ozone has been the focus of considerable interests. The results of early studies led to computed PA values from 124 to 157 kcal mol^{-1}, depending on the level of theory employed.[4-6] More recently, two high-level theoretical studies, performed at the CCSDT[7] and the LCGTO-DF[8] level, gave PA values of 148.0 and 149.4 kcal mol^{-1}, respectively, not only mutually consistent but in excellent agreement with the experimental measurements.[2-3]

From the above, it appears that the alleged lack of data, complained by MLHLBT, on a fundamental property of O_3, such as its basicity, is not entirely borne out by an examination of the available literature. Furthermore, the available data appear, in principle, more reliable than those reported in reference 1, since they deal with *isolated* HO_3^+ ions, as found in low-pressure gas-phase experiments and considered in theoretical studies, unaffected by the adventitious interactions with a dense environment. The problem arises as regards to the degree of agreement between the available theoretical[7,8] and experimental data[2,3] and the salient conclusions reached by MLHLBT, namely that CO appears slightly *more* basic than O_3 and this latter significantly *more* basic than COS (basicity order:CO>O_3>COS). From the available gas-phase thermochemical data, it comes out instead that there is an appreciable, if not very large PA difference among the above compounds, and, more importantly, that *the basicity order is actually reversed* (basicity order:COS≥O_3>CO). Indeed, the PA of COS, O_3, and CO amount to 150.0±2, 148±3, and 141.9±2 kcal mol^{-1}, respectively.[9,10] Direct experimental evidence on this point is provided by the absolute inefficiency of the proton transfer from HO_3^+ to CO (point **e** in Figure 1), which under the conditions prevailing in the FTICR-MS experiments, denotes the endothermic character of the process and hence *a PA of O_3 higher than that of CO.*

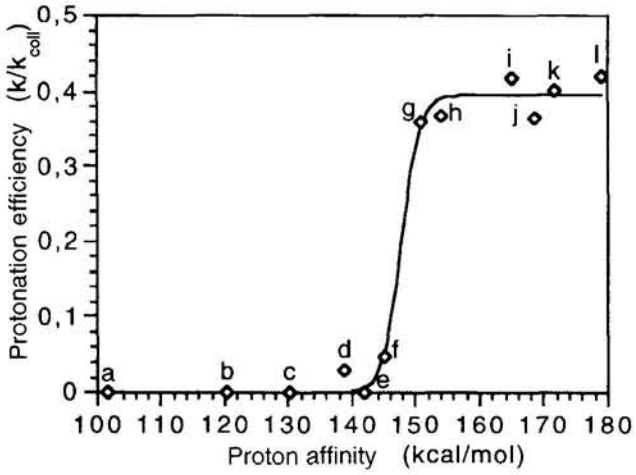

Figure 1. Collision efficiency (k/k_{coll}) for the proton transfer from HO_3^+ to different gaseous base: Kr (a), Xe (b), CH_4 (c), N_2O (d), CO (e), CH_3F (f), SO_2 (g), C_2H_2 (h), H_2O (i), H_2S (j), CH_2O (k), HN_3 (l). k denotes the experimental proton transfer rate constant, k_{coll} the corresponding collison rate constant, estimated according to the trajectory calculation method (reference 11). The plot includes data from references 2 and 3.

A likely reason for the above discrepancy may be found in the establishment of different cooperative interactions of the rest of the O_3 and CO structures with the crystal lattice of the zeolites on top of the hydrogen bonding with their hydroxyl groups,[12] which may appreciably affect the intrinsic basicity of the two molecules.

As a final, the available theoretical and gas-phase experimental results concur with MLHLBT's conclusions that terminal atoms are the most basic site of O_3.

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