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Reply to "Comment on 'Role of (NO)₂ Dimer in Reactions of Fe⁺ with NO and NO₂ Studied by ICP-SIFT Mass Spectrometry'"

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Supporting Information

We respond here to the Comment of Melko et al.,¹ henceforth designated as Vetal 2013, that has critiqued our recent publication on the "Role of (NO)₂ Dimer in Reactions of Fe⁺ with NO and NO₂ Studied by ICP-SIFT Mass Spectrometry".² Our response is brief; the Supporting Information provides more detail.

■ BRANCHING RATIO ANALYSIS

Vetal 2013 continue to discount the straightforward analysis of our observed ion reaction profiles and ion product distribution for the reaction of Fe⁺ with NO₂ on the basis of modeling that is somewhat arbitrary and, more significantly, completely ignores important low flow data points. We note that our fitting procedure in our previous² Figure 1 relies on standard kinetic equations and does not impose prejudged rate coefficients; rather, our procedure determines rate coefficients from the best fits to the experimental data.² The fits in the ion branching ratio analysis are based on the same kinetic equations as applied in the fitting of the ion reaction profiles. Also, we emphasize that the zero intercept for NO⁺ formation in the raw branching ratio data in the RHS of our previous² Figure 1 provides unambiguous evidence for the absence of primary NO⁺ formation. Primary NO⁺ formation therefore was not included in the kinetic equations used for the fits. No low flow data points were ignored.

■ NO₂ IMPURITY ANALYSIS AND MONITOR REACTIONS

In previous publications we have used monitor reactions of atomic metal and metal oxide cations to estimate upper limits to possible NO₂ impurities in the NO used in our investigations of reactions of atomic metal cations with NO. Known ion products for reactions of ions with NO₂ allows them to be used as signature ions for NO₂ impurities in the studies of NO chemistry, at least in principle, when the NO₂ reaction is fast and when the NO₂ and NO chemistries lead to different ion products. We have described such an approach for reactions with several atomic metal ions in ref 2 and some metal oxide ions in ref 3. In their Comment, Vetal 2013 have critiqued our use of the reactions of Hg⁺, Ge⁺, and As⁺ that we described in our 2013 paper.² A number of unfortunate typographical errors in our work were discovered by these authors in the process and attention was drawn by them to the importance of the electron transfer reaction between NO₂⁺ and NO that can limit

the use of NO₂⁺ as a monitor ion. Our typographical errors are addressed in the Supporting Information, as is the importance of the electron transfer reaction between NO₂⁺ and NO in our use of reactions of Hg⁺, Ge⁺ and As⁺.

Our experience now indicates, and we thank Vetal 2013 for their valuable input in this regard, that the occurrence of the further reaction of NO₂⁺ with NO, not to mention the presence of background signal, will almost invariably limit the level of detection of NO₂ impurity in NO to about 1.0 or 1.5% in our experiments.

■ ROLE OF NO₂ IMPURITIES IN THE NO EXPERIMENTS

As regards the role of NO₂ impurities in our NO experiments, we now recognize that the presence of NO₂ impurity can obfuscate the analysis of the kinetics of slow reactions of atomic metal cations to produce NO⁺ and MO⁺, ascribed by us to second-order NO chemistry,³ as these ions are also observed (as primary or secondary products) for the reactions of these atomic cations with NO₂.⁴ On the other hand, slow reactions of atomic metal cations with a possible NO₂ impurity will be less obfuscating in measurements of slow reactions of atomic metal cations with NO. A noteworthy example is the reaction of Ni⁺ that is described below.

■ ROLE OF (NO)₂ DIMER IN THE NO EXPERIMENTS

As we have mentioned previously,² the presence of any (NO)₂ dimer in the added NO would also introduce complications into the elucidation of the NO reaction kinetics. Although the equilibrium concentration of the dimer is expected to be low at the low He pressure (0.35 Torr) within the reaction region of our SIFT, we are not convinced that the dimer can be ruled out completely as a contributing component of the NO that emerges from the NO inlet; equilibrium may not prevail in the NO inlet, and the lifetime of the (NO)₂ dimer is still somewhat uncertain.

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■ ROLE OF SECOND-ORDER NO CHEMISTRY IN THE NO EXPERIMENTS

We appreciate the modeling scenario presented by Vetal 2013 for the reaction of Fe^+ with NO from which they conclude that second-order NO rates of reaction are “immeasurably slow” ($k < 5 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), 5 orders of magnitude lower than what we reported. The model insists on the attainment of equilibrium concentrations of the FeNO^+ intermediate. This assumption is unrealistic in our opinion; we expect the reaction kinetics to be controlled by the collision rate of Fe^+ with NO to produce the $[\text{FeNO}^+]$ and the lifetime of this intermediate against back-dissociation, which is not well-known. Any subsequent collision of $[\text{FeNO}^+]$ with NO would lead to second-order (in NO) kinetics.

Although the presence of NO_2 impurities in NO is likely to obfuscate measurements of the kinetics of reactions of metal cations with NO when the reaction with NO_2 is fast ($k = 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), no such problems exist when the NO_2 reaction is slow (e.g., $k = 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). We have six examples (Ni^+ , Cu^+ , Rh^+ , Pd^+ , Ag^+ , and Cd^+) for which reactions with possible NO_2 impurity are slow and therefore negligible.⁴ Figure 1 shows reactions of Ni^+ with NO_2 and

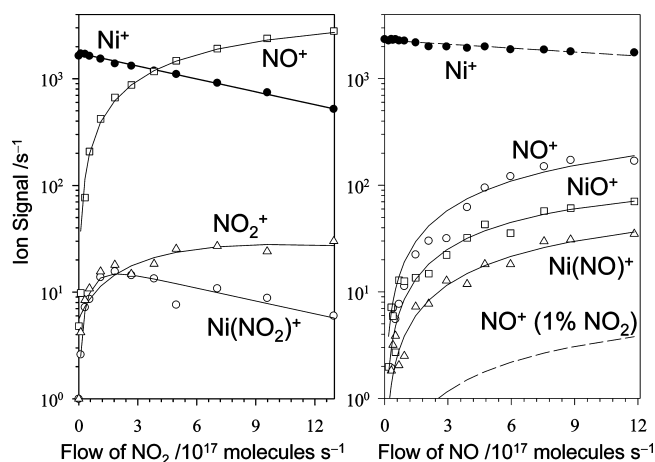


Figure 1. Measured profiles for reactions of Ni^+ with NO_2 (LHS) and NO (RHS). The rate coefficients for the two reactions are comparable at 2.2×10^{-11} and $1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively. The dashed line in the NO profile (RHS) represents the possible NO^+ contribution by a 1% NO_2 impurity in NO.

NO ,^{4,3} which proceed with very similar rates. The NO reaction profile shows that the NO^+ produced by possible NO_2 impurity of 1% can be ignored. This and other similar results clearly demonstrate the occurrence of second-order chemistry (in NO) either by sequential collisions with NO or collisions with $(\text{NO})_2$ dimer. Apparent trends in reaction efficiency of individual channels and ratios in $k(\text{NO})/k(\text{NO}_2)$ as identified by Vetal 2013¹ therefore should be interpreted with this in mind. The situation can be somewhat complex if NO_2 impurities and second-order chemistry (either by two sequential NO collisions or by collision with $(\text{NO})_2$ dimer) occur concomitantly.

■ ASSOCIATED CONTENT

Supporting Information

Full description of the reply. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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