A MODEL FOR THE PRODUCTION OF CHEMICAL NON-MASS-DEPENDENT OXYGEN ISOTOPE EFFECTS.

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Given the ubiquity of non-mass-dependent (NoMaDic) oxygen isotopic compositions in meteorites(1), it is clearly important to study chemical mechanisms which might be relevent for their production. It was reported two years ago(2) that NoMaDic effects are produced in the synthesis of ozone via an electrical discharge through molecular oxygen. We have extended these studies to other molecules(3), as well as detailed the kinetics and the functional dependencies of the effect(4). This work has allowed us to restrict the mechanistic step responsible for the effect and propose a model.

It was originally suggested(2) that the NoMaDic effect was produced during the electron impact dissociation of O_2, presumably through the process of isotopic self shielding. It was subsequently pointed out that this could not be the case, since oxygen atom-molecule isotopic exchange, a process kinetically faster than three body ozone formation and distinctly mass dependent, would obscure any effect produced during O_2 dissociation(5,6). Even though this argument may not be completely valid under our low temperature experimental conditions, we have been able to show, using CO_2 dissociation experiments(3), that the basic conclusion is relevent, viz. the NoMaDic effect does not occur in the O_2 dissociation step.

Using kinetic data(4) we have been able to show that under the relevent experimental conditions, O_3 formation takes place by a mechanism much simpler than the classical Chapman system.

(i) $O_2 + e \longrightarrow O + O + e$

(ii) $O + O_2 \longleftrightarrow O_3^*$

(iii) $O_3^* + \text{Wall} \longrightarrow O_3\text{-Wall}$

The result is that all O_3 is formed on the walls of the reaction vessel. It has already been shown that the first step of this mechanism is not be responsible for the effect, the same is true for the last step, O_3 stabilization and trapping, due to its near unit efficiency. Therefore, the NoMaDic effect is restricted to the formation or destruction of the O_3^* metastable transition state.

A model of the process responsible for this phenomenon has been produced based on the following assumptions: 1)The probability of a reactive intermediate being quenched by collision with a third body (of the type $O + O_2 \longrightarrow O_3^* + \text{Wall} \longrightarrow O_3\text{-Wall}$) is equal to the collision rate times the lifetime of the intermediate (τ). 2)The collision rate is weakly related to isotopic substitution. 3)The observed isotope effect, with $\delta^{17}O = \delta^{18}O$, may be explained if the lifetimes of the O_3^* intermediates containing ^{17}O or ^{18}O ($^{17}\tau$ and $^{18}\tau$) are equal and greater than the lifetime for the species containing only ^{16}O (τ).

A mechanism for producing the isotopic dependence in τ is available, based on molecular symmetry arguments. The metastable species lifetime is greatly increased when the oxygen atom and molecule reactants have exactly the correct total energy to match one of the diffuse energy states near the ozone dissociation limit(7). The metastable ozone lifetime is strongly dependent on the number of available energy states, which is partially determined by the symmetry properties of the product molecule. The isotopically substituted ozone molecules may have either C_{2v} (X-Y-X) or C_s (Y-X-X) symmetry. All of the C_{2v} species possess half their compliment of rotational states(8), whereas the C_s species possess their full compliment. Since only the O_3^* species containing the heavy isotopes have representatives of the latter group, this reservior will be enriched in the reaction products due to the greater number of available states.

This model possesses three important implications. First, since the effect is not produced during the dissociation of O_2, it should be observable, independent of whether the source of oxygen atoms is provided by ultraviolet radiation, electron impact or any other dissociative process. Second, the process should result in an overabundance of the products with C_s symmetry. Finally, the effect is not restricted to ozone formation, as there are several systems which satisfy its basic constraints. The

criteria for producing a NoMaDic effect of the type reported include: 1)the reaction occurs in the gas phase, 2)the reaction intermediate must be subject to the symmetry restriction discussed, and 3)the reaction products need to be chemically or physically separable, at least to the extent that further reaction and superposition of further isotopic effects is avoided. As a specific example, the reaction of carbon monoxide with oxygen atoms to form CO_2 would be a viable candidate system.

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