DO LARGE RATE COEFFICIENTS FOR ION-POLAR NEUTRAL REACTIONS HAVE A SERIOUS EFFECT ON CHEMICAL MODELS OF DENSE CLOUDS?

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Adams, Smith, and Clary (1985) have recently argued that rate coefficients for ion-polar neutral gas phase reactions occurring at interstellar cloud temperatures (<100 K) are considerably larger than the canonical Langevin value. While their conclusion is based primarily on the theoretical work of Clary (1985), a variety of previous theoretical treatments (see, e.g., Bates 1982) support this view. Herbst (1986) has noted, however, that all of these treatments consider the long-range attractive ion-dipole potential only and ignore possible short-range repulsive effects. If the long-range theories are correct, rate coefficients as large as 1x10(-07) cc/sec (two orders of magnitude greater than the Langevin value) can be expected at a temperature of 10 K. Although there is as yet little experimental evidence concerning the reliability of the calculated rates at temperatures below 100 K, it is important to determine the effect of such large rate coefficients on gas phase chemical models of dense interstellar clouds.

In order to incorporate large ion-polar neutral rate coefficients into existing gas phase reaction networks, it is necessary to utilize simplified theoretical treatments because of the significant number of rate coefficients needed. We (Herbst and Leung 1986a) have used two simple theoretical treatments - the "locked dipole" approach of Moran and Hamill (1963) for linear polar neutrals and the "trajectory scaling" approach of Su and Chesnavich (1982) for non-linear polar neutrals. The former approach is suitable for linear species because in the interstellar medium these are rotationally relaxed to a large extent and the incoming charged reactants can "lock" their dipoles into the lowest energy configuration. The latter approach is a better approximation for non-linear neutral species, in which rotational relaxation is normally less severe and the incoming charged reactants are not as effective at "locking" the dipoles. The treatments are in reasonable agreement with more detailed long-range theories and predict an inverse square root dependence on kinetic temperature for the rate coefficient. Compared with the "locked dipole" method, the "trajectory scaling" approach results in rate coefficients smaller by a factor of approximately 2.5.

The calculated large rate coefficients have been incorporated into the gas phase chemical model of Herbst and Leung (1986b) which contains 206 chemical species and 1958 reactions, and is pseudo time-dependent in the sense that physical conditions are assumed to remain constant as the chemistry evolves from given initial conditions. The changes found from previous results are less than dramatic. In our previous work (Herbst and

Leung 1986b; Leung, Herbst, and Huebner 1984) it was found that the calculated abundances of complex species peak at times earlier than that required for steady state to be achieved. This feature is preserved in the present calculation. In general, however, stable polar neutral species show decreases in their calculated abundances at both "early" times, when peak abundances are achieved, and at steady state of up to one order of magnitude. Most neutral atoms, stable nonpolar species, reactive neutral species (radicals), and some molecular ions deviate from this trend and show abundances that are unchanged from previous results or that actually increase. In addition, the use of the more rapid rates speeds up the chemistry of stable polar neutrals such as HC_3N resulting in the achievement of peak abundances at earlier times than in previous calculations. All of these changes are found to be stronger in our models of dark clouds, where the temperature is typically 10 K, than in our models of warmer sources such as OMC-1.

The decreases in calculated abundances of stable polar species are often coupled with increases in the calculated abundances of protonated ions of these species, as originally noted for CS and HCS+ by Millar et al. (1985). These authors showed via a small reaction network that the observed value of the abundance ratio HCS+/CS in both TMC-1 and Sgr B2 can only be accounted for if the rapid ion-polar neutral rates are utilized. Their results are in reasonable but not perfect agreement with our detailed model results. Our new results also show a considerable enhancement in the HCNH+/HCN ratio, which may explain the recent observation of HCNH+ (Ziurys and Turner 1985). Despite the sensitivity of these ion/neutral abundance ratios to the size of ion-polar neutral rate coefficients, we find that overall the agreement between model results and observation is not changed appreciably by adoption of the larger rate coefficients.

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