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EFFECTS OF LARGE RATE COEFFICIENTS FOR ION-POLAR NEUTRAL REACTIONS ON CHEMICAL MODELS OF DENSE INTERSTELLAR CLOUDS

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ABSTRACT

Pseudo–time-dependent models of the gas phase chemistry of dense interstellar clouds have been run with large rate coefficients for reactions between ions and polar neutral species, as advocated by Adams, Smith, and Clary. The higher rate coefficients normally lead to a reduction in both the peak and steady state abundances of polar neutrals, which can be as large as an order of magnitude but is more often smaller. Other differences between the results of these models and previous results are also discussed.

Subject headings: interstellar: molecules — molecular processes

I. INTRODUCTION

Following work by Sakimoto (1980) and Takayanagi (1982), Adams, Smith, and Clary (1985) have recently argued that, at the low temperatures (10–50 K) of dense interstellar clouds, ion-molecule reactions involving polar neutrals should occur with rate coefficients one to two orders of magnitude larger than the canonical value of 10^{-9} cm^3 s^{-1} predicted by the Langevin theory. If experimentally confirmed, this might have very important implications for chemical models of dense clouds. The conclusion of Adams, Smith, and Clary (1985) is based partially on a new long-range theory (one which considers only the long-range, ion-polar neutral attractive potential) of Clary (1985) and partially on some experimental evidence involving proton transfer reactions over the temperature range 205–540 K. Other recent theoretical treatments of ion-polar reactions involving the long-range potential only include those of Sakimoto and Takayanagi (1980); Chesnavich, Su, and Bowers (1980); Celli, Weddle, and Ridge (1980); Bates (1982); and Su and Chesnavich (1982). These treatments also yield large rate coefficients in the 10–50 K temperature range although the calculations of Clary (1985) appear to give the largest rate increases. While there has been little experimental information available at temperatures under 80 K, recent work by Rowe (1985, as reported in private communications in Adams, Smith, and Clary 1985 and to E. Ferguson) shows that at 28 K reactions involving the ions He^+, C^+, and N^+ and the polar neutrals H_2O and NH_3 proceed much more rapidly than at room temperature. Although it is not clear that long-range theories are uniformly correct in their predictions of large rates for all reactions involving ions and polar neutral molecules at low temperature (short-range repulsive effects may occur; see Herbst 1986), it is important to determine the effect of such large rate coefficients on chemical models of dense interstellar clouds.

In this paper, we report the results of model calculations on dense interstellar clouds with the inclusion of large ion-polar neutral rates. The basic model utilized is that of Leung, Herbst, and Heubner (1984), with the reaction network as updated by Herbst and Leung (1986). The interested reader is referred to this latter paper for details. In addition to updating the reaction network, Herbst and Leung (1986) studied the cloud chemistry as a function of visual extinction, cloud temperature, and carbon-to-oxygen ratio. The model currently contains 206 chemical species and 1958 reactions and is pseudo–time-dependent in that the physical conditions (e.g., gas density, temperature, and visual extinction) are assumed to be constant so that the calculation simply follows the chemical evolution of a cloud of constant mass. A representative sample of complex molecular species is contained in the model.

II. RATE COEFFICIENTS UTILIZED

The theories of Clary (1985) and others are normally too complex for facile inclusion into a large model calculation. We have therefore adopted two simpler theoretical treatments, which closely approximate the more refined long-range theories in the 10–50 K range. A distinction has been made between linear and nonlinear neutral polar reactants. The former have been assumed to be relaxed rotationally under the low density conditions of dense clouds. Under these circumstances, the "locked dipole" model of Moran and Hamill (1963) is appropriate and closely resembles the $J = 0$ (complete rotational relaxation) result tabulated by Adams, Smith, and Clary (1985). In this model, the rate coefficient $k_{\rm LD}$ (the subscript LD stands for "locked dipole") is given by the expression

$$k_{\rm LD} = \{1 + [2/(\pi)^{1/2}]x\}k_{\rm L} . \qquad (1)$$

Here $k_{\rm L} = 2\pi e(\alpha/\mu)^{1/2}$ is the standard, temperature-independent Langevin expression, and $x = \mu_D/[2\alpha kT]^{1/2}$, where μ is the reduced mass in the collision, e is the electronic charge, μ_D is the dipole moment of the neutral reactant, α is its polarizability, and k is the Boltzmann constant.

For reactions involving nonlinear polar molecules, we have chosen to use the trajectory scaling approach of Su and Chesnavich (1982) because the frequent existence of metastable states results in less rotational relaxation and less "dipole locking." In this case the rate coefficient $k_{\rm TS}$ (the subscript TS stands for "trajectory scaling") is given by the expression

$$k_{\rm TS} = (0.62 + 0.4767x)k_{\rm L} . \qquad (2)$$

Relation (2) is found by performing classical trajectory calculations and fitting the results for the rate coefficient to a functional form of the type $k = (a + bx)k_L$. This formula is in agreement with perturbed rotational state calculations (Sakimoto 1985) for ion-symmetric top collisions and results in somewhat smaller rate coefficients than the "locked dipole" approach. Because it is important to use k_{LD} or k_{TS} only when x is large (for example, if $T = 10$ K, $\alpha = 1$ Å^3, and $\mu_D = 3$ debye, then $x = 57$) and the rate coefficients far exceed the Langevin value, we can further simplify equations (1) and (2) by ignoring the constant factor multiplying k_L. This results in forms for k_{LD} and k_{TS} that are compatible with those for other rate coefficients in our current model program. Both simplified expressions yield a dependence of $T^{-1/2}$ for the rate coefficient and can result in rate coefficients approaching 10^{-7} cm^3 s^{-1} at 10 K for sufficiently polar neutrals and light ions.

Equations (1) and (2) have been utilized to estimate rate coefficients for all ion-polar neutral reactions in our model involving major ions (e.g., those that do not react rapidly with H_2). These ions are H^+, He^+, C^+, Si^+, S^+, Mg^+, $H_3{}^+$, HCO^+, N_2H^+, H_3O^+, $CH_3{}^+$, $C_2H_2{}^+$, $C_2H_3{}^+$, HNO^+, $HCNH^+$, $NH_3{}^+$, $HCO_2{}^+$, OCS^+, $CH_5{}^+$, C_3H^+, $C_2H_4{}^+$, and H_3CO^+. Other major ions not included in this list are those which do not react with polar neutrals in our model. All permanent dipole moments needed in the estimation of rate coefficients are given either in Table 1 of this paper or Table 1 of Adams, Smith, and Clary (1985). Polarizabilities α are not needed to determine k_{LD} or k_{TS} because the $(\alpha)^{1/2}$ factor in the Langevin rate coefficient k_L cancels the $(\alpha)^{-1/2}$ factor in x. If a calculated rate coefficient was found to be smaller than k_L (which could happen for a sufficiently small dipole moment) the Langevin value was used.

Herbst (1986) has argued that equations (1) and (2) may well lead to overly large rate coefficients at low temperatures for reactions that are slower at room temperature than predicted by long-range theories. Unfortunately, this possibility can only be verified with knowledge of the potential surface for individual reactions. Since this knowledge is extremely limited, we have chosen to adopt equations (1) and (2) for all ion-polar reactions. The justification is to determine the maximum possible effects due to these large rates.

In addition to using large rate coefficients for ion-polar neutral reactions, we have adopted the new low value for the dissociative electron recombination of HCS^+ (Millar *et al.* 1985) and have deleted the endothermic reaction $N + H_3{}^+ \rightarrow NH^+ + H_2$ from the reaction network of Herbst and Leung (1986).

TABLE 1

PERMANENT DIPOLE MOMENTS μ_D (debyes) OF SOME INTERSTELLAR MOLECULES

Molecule	Value	Reference
CH	1.46	1
CO	0.112	2
NO	0.153	2
SiS	1.73	1
SiH	0.3	3
MgH	1.283	4
NS	1.81	1
NH_2	1.83	5
HCO	~1	
NaOH	~5	
HNO	1.67	6
CCCH	3.1	7
CCCO	2.39	8
C_3H_2	3.3	9
CH_3N	2.0	10
C_3H_3	3.998	11
C_3H_4	0.781	2
NH	1.3	12
CN	1.45	1
SiC	~2	
SiO	3.089	1
NaH	6.7	13
HS	0.76	1
CH_2	0.8	14
NCO	0.64	15
CCH	0.8	16
CCN	1.3	7
H_2CS	1.647	17
CCCN	2.2	18
C_2H_3	~1.5	
C_4H	0.9	18
C_4N	~1.8	
C_5N	~2.7	
HC_5N	4.33	19

NOTE.—Dipole moments for additional molecules are given by Adams, Smith, and Clary 1985.

REFERENCES.—(1) Huber and Herzberg 1979. (2) Nelson, Lide, and Maryott 1967. (3) Cade *et al.* 1969. (4) Meyer and Rosmus 1975. (5) Brown and Williams 1973. (6) Saito and Takagi 1972. (7) Green 1980. (8) Brown *et al.* 1983. (9) Lee, Bunge, and Schaeffer 1985. (10) Kirchhoff, Johnson, and Lovas 1973. (11) Ha, Graf, and Gunthard 1973. (12) Silk and Murrell 1970. (13) Sachs, Hinze, and Sabelli 1975. (14) Del Bene 1971. (15) Lovas 1978. (16) Green as reported by Tucker, Kutner, and Thaddeus 1974. (17) Johnson, Lovas, and Kirchhoff 1972. (18) Wilson and Green 1977. (19) Snyder, Dykstra, and Bernholdt 1986.

III. DISCUSSION OF RESULTS

Table 2 contains a representative sample of calculated fractional abundances (relative to H_2) for our standard model of TMC-1 [total gas density $n_T \equiv n(H) + 2n(H_2) = 2 \times 10^4$ cm^{-3}; gas kinetic temperature $T = 10$ K; "low metal" abundances; visual extinction $A_V = 500$]. Shown in the table are previous results with low ion-polar rate coefficients taken from Herbst and Leung (1986) and the new results. For each model, two sets of calculated fractional abundances are given. The first set corresponds to an "early time" at which the abundances of complex molecules are at or near their peak values (see below). The "early time" of the previous calculation is at 3.2×10^5 yr while it is at 1.0×10^5 yr for the new calculation. The second set corresponds to abundances at steady state ($> 10^7$ yr). A glance at Table 2 shows that differences of up to an order of magnitude exist both at "early time" and at steady state between our previous and current model results. In general, neutral diatomic and polyatomic species *decrease* in abundance when the rapid ion-polar neutral rates are utilized, many by factors of less than 3 or so but a few (especially the more complex, polar molecules) by factors of up to one order of magnitude. Most neutral atoms; stable nonpolar species such as CH_4, C_2H_2, and C_2H_4; some sulfur-containing species such as OCS, SO, H_2S, and HS; some polar radicals; and some molecular ions deviate from this trend and possess increased abundances at "early time" and/or steady state. Overall, the number of species in Table 2 with reduced abundances in the new model exceeds the number of species with increased abundances for both the "early time" results and at steady state, while fewer than 10% of the species have the same abundances in both models.

TABLE 2

SELECTED CALCULATED ABUNDANCES RELATIVE TO H_2

Chemical Species	Previous Results (n = 2.0(04); T = 10 K; A_v = 500)		New Results		Chemical Species	Previous Results		New Results	
	Early 3.2(5) yr	St. State >1.0(7) yr	Early 1.0(5) yr.	St. State >1.0(7) yr.		Early	St. State	Early	St. State
H	1.6(-04)	1.1(-04)	2.2(-04)	1.1(-04)	He	2.8(-01)	2.8(-01)	2.8(-01)	2.8(-01)
C	5.7(-06)	2.0(-09)	5.8(-05)	7.7(-09)	N	3.6(-05)	1.5(-06)	4.2(-05)	2.7(-06)
O	2.0(-04)	3.6(-05)	2.7(-04)	7.5(-05)	Si	5.6(-09)	4.9(-09)	1.5(-08)	1.5(-08)
S	1.4(-08)	5.4(-09)	7.9(-08)	4.5(-08)	Fe	1.4(-09)	1.3(-09)	1.2(-09)	1.6(-09)
Na	1.3(-09)	1.2(-09)	1.1(-09)	1.3(-09)	Mg	5.6(-09)	4.7(-09)	4.4(-09)	4.9(-09)
H_2	1.0(-00)	1.0(-00)	1.0(-00)	1.0(-00)	C_2	7.0(-09)	1.2(-10)	3.2(-08)	3.1(-10)
N_2	2.2(-06)	2.0(-05)	1.7(-07)	2.0(-05)	O_2	4.4(-06)	8.2(-05)	4.6(-07)	6.5(-05)
CH	6.3(-09)	4.7(-10)	5.0(-08)	2.1(-10)	NH	2.5(-08)	1.3(-08)	5.2(-09)	3.9(-09)
OH	2.0(-07)	6.5(-07)	8.9(-08)	2.5(-07)	CO	1.3(-04)	1.5(-04)	8.2(-05)	1.5(-04)
CN	8.1(-08)	3.2(-09)	1.3(-07)	6.0(-09)	NO	1.6(-07)	3.0(-07)	2.3(-08)	1.9(-07)
SiC	3.0(-11)	2.4(-12)	2.9(-11)	1.4(-12)	SiS	5.2(-11)	1.2(-11)	1.1(-11)	7.3(-12)
SiO	1.0(-08)	1.1(-08)	7.4(-10)	7.0(-10)	SiH	1.9(-11)	2.3(-10)	1.6(-11)	2.0(-10)
NaH	2.3(-12)	2.1(-12)	2.8(-13)	2.2(-13)	MgH	1.5(-12)	1.3(-12)	1.3(-12)	6.9(-13)
HS	5.2(-12)	3.4(-12)	1.2(-11)	7.7(-12)	CS	4.2(-08)	4.8(-08)	9.9(-09)	1.4(-08)
NS	7.3(-10)	3.8(-11)	1.4(-10)	8.7(-12)	SO	2.6(-09)	1.2(-08)	1.1(-09)	2.0(-08)
NaOH	8.6(-13)	4.5(-13)	1.3(-13)	5.5(-14)	CH_2	7.0(-08)	1.2(-09)	3.3(-07)	8.3(-10)
NH_2	2.9(-07)	1.1(-07)	9.1(-08)	5.3(-08)	H_2O	7.8(-06)	3.6(-06)	2.4(-06)	1.3(-06)
HCN	4.9(-07)	5.5(-09)	1.7(-07)	2.6(-09)	HNC	4.9(-07)	5.9(-09)	1.1(-07)	2.9(-09)
HCO	9.0(-10)	9.4(-11)	2.3(-09)	7.1(-11)	C_2H	6.2(-09)	2.4(-10)	8.0(-08)	1.7(-10)
CO_2	5.2(-07)	2.6(-07)	3.5(-07)	1.6(-07)	OCN	4.7(-09)	4.6(-08)	1.6(-10)	2.7(-08)
H_2S	5.9(-11)	1.1(-10)	4.5(-11)	2.1(-10)	OCS	9.5(-08)	4.6(-08)	6.7(-08)	7.0(-08)
SO_2	3.1(-09)	4.8(-08)	3.7(-10)	1.0(-08)	H_2CO	3.9(-07)	7.7(-09)	1.9(-07)	2.3(-09)
NH_3	9.3(-07)	1.8(-07)	2.1(-07)	8.7(-08)	C_2H_2	4.3(-07)	3.8(-09)	9.5(-07)	9.9(-09)
C_3O	3.4(-11)	4.9(-12)	2.8(-11)	3.4(-12)	CH_3	1.7(-09)	2.9(-10)	2.7(-09)	1.5(-10)
CH_4	1.5(-06)	6.8(-08)	1.3(-06)	1.1(-07)	C_3	3.0(-09)	3.3(-11)	1.3(-08)	3.0(-11)
HC_3N	2.4(-8)	3.5(-12)	6.4(-09)	1.6(-12)	H_2CS	2.0(-09)	2.7(-11)	1.9(-09)	3.5(-11)
C_2H_3N	1.1(-07)	1.5(-11)	1.3(-08)	1.6(-12)	CH_3OH	4.0(-08)	5.6(-10)	1.1(-08)	6.1(-11)
HNO	1.9(-09)	7.6(-11)	3.8(-10)	3.8(-11)	C_2N	3.8(-09)	1.2(-11)	6.3(-09)	1.3(-11)
C_3H	2.1(-07)	8.5(-10)	1.8(-08)	6.5(-11)	C_3N	2.0(-09)	1.7(-12)	3.3(-09)	2.9(-12)
C_4	2.0(-09)	4.4(-12)	1.1(-08)	5.3(-12)	C_2H_3	1.2(-07)	1.1(-09)	6.8(-08)	3.9(-10)
CH_2O_2	2.3(-08)	2.0(-08)	2.0(-09)	3.1(-09)	C_4H	1.3(-07)	6.6(-12)	1.0(-07)	2.5(-12)
C_4N	2.9(-11)	2.5(-16)	9.9(-11)	1.4(-15)	C_2H_4	2.5(-09)	2.6(-12)	2.6(-09)	7.2(-12)
C_3H_2	1.4(-07)	4.4(-10)	2.8(-08)	8.5(-11)	C_5N	2.8(-11)	2.5(-16)	9.9(-11)	1.4(-15)
CH_5N	7.4(-08)	4.1(-10)	1.3(-08)	6.1(-11)	C_3H_3	9.1(-10)	1.9(-12)	2.3(-10)	3.0(-13)
C_2H_4O	5.1(-08)	2.4(-09)	9.5(-09)	4.4(-10)	HC_5N	5.3(-10)	8.9(-16)	1.4(-10)	4.3(-16)
CH_3OCH_3	2.1(-09)	6.3(-13)	2.9(-10)	2.3(-14)	C_2H_5OH	8.7(-10)	7.3(-13)	1.0(-10)	1.6(-13)
CH_3N	1.1(-07)	7.5(-10)	1.7(-08)	8.9(-11)	C_3H_4	5.6(-10)	1.3(-12)	1.7(-10)	9.2(-13)
C_4H_2	6.6(-08)	6.1(-12)	1.5(-07)	1.7(-11)	C_2H_2O	1.6(-07)	7.0(-09)	7.8(-08)	1.7(-09)
e	3.4(-08)	3.5(-08)	3.4(-08)	3.3(-08)	H^+	3.5(-10)	2.3(-10)	1.8(-10)	1.8(-10)
He^+	7.3(-10)	5.1(-10)	4.8(-10)	3.1(-10)	C^+	3.7(-09)	1.1(-09)	1.7(-09)	1.3(-09)
S^+	1.4(-10)	4.5(-11)	7.7(-11)	9.3(-11)	Fe^+	4.6(-09)	4.7(-09)	4.8(-09)	4.4(-09)
Na^+	2.7(-09)	2.8(-09)	2.9(-09)	2.7(-09)	Mg^+	8.4(-09)	9.3(-09)	9.6(-09)	9.1(-09)
CO^+	8.3(-15)	3.6(-14)	4.2(-15)	3.7(-14)	NO^+	2.4(-12)	2.9(-12)	8.7(-13)	3.7(-12)
SO^+	4.0(-12)	6.9(-12)	1.2(-11)	4.1(-11)	H_3^+	2.4(-09)	3.4(-09)	1.6(-09)	1.8(-09)
HCO^+	5.4(-09)	1.0(-08)	4.4(-09)	9.4(-09)	HOC^+	5.7(-10)	3.0(-10)	5.4(-10)	3.7(-10)
HNO^+	7.1(-12)	1.9(-11)	8.1(-13)	5.5(-12)	N_2H^+	4.0(-11)	5.0(-10)	2.0(-12)	2.8(-10)

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TABLE 2—*Continued*

Chemical	Previous Results		New Results		Chemical	Previous Results		New Results	
Species	Early	St. State	Early	St. State	Species	Early	St. State	Early	St. State
$HSiO^+$	4.9(-12)	4.0(-12)	1.1(-11)	1.2(-11)	HCS^+	5.9(-12)	1.4(-11)	1.5(-11)	6.6(-11)
NH_3^+	2.7(-11)	4.4(-12)	1.9(-11)	7.2(-12)	CH_3^+	9.9(-11)	4.0(-12)	4.6(-10)	5.0(-12)
H_3O^+	2.6(-09)	1.5(-09)	2.4(-09)	2.0(-09)	H_2CN^+	3.0(-10)	7.4(-12)	7.5(-10)	3.4(-11)
$C_2H_2^+$	1.0(-11)	9.6(-14)	9.4(-11)	2.2(-13)	HCO_2^+	8.1(-12)	6.2(-12)	3.4(-12)	2.1(-12)
NH_4^+	8.5(-10)	1.7(-10)	6.2(-10)	2.8(-10)	$C_2H_3^+$	1.0(-10)	2.5(-12)	9.0(-11)	3.9(-12)
$C_3H_2^+$	3.4(-11)	2.9(-13)	1.1(-10)	5.3(-13)	OCS^+	5.9(-11)	2.4(-11)	1.9(-10)	2.5(-10)
$HOCS^+$	1.5(-11)	1.2(-11)	6.2(-11)	1.1(-10)	CH_5^+	7.3(-11)	4.3(-12)	1.7(-10)	4.3(-12)
$C_4H_2^+$	3.7(-11)	2.5(-15)	3.6(-10)	7.2(-15)	$C_3H_2N^+$	5.0(-11)	9.7(-15)	1.2(-10)	4.2(-14)

NOTE.—All numbers in the table follow the convention $a(-b)$ signifies $a \times 10^{-b}$.

To demonstrate the major effects of large rate coefficients for ion-polar neutral reactions in some detail, we use the highly polar molecule HC_3N as an example. Figure 1 shows the fractional abundance of HC_3N as a function of time for our previous model of TMC-1 and for this same model with rate coefficients for ion polar-neutral reactions given by equations (1) and (2). In both models, the calculated HC_3N abundances follow the now familiar pattern for complex molecules of peaking at times well before steady state is achieved (Leung, Herbst, and Huebner 1984). It can be seen that the higher rates speed up the chemistry of HC_3N such that its peak abundance is reached earlier. (This effect has necessitated our using different "early times" for the two models.) In addition, the more rapid rates lead to a reduction in both the peak and steady state abundances by about a factor of 3, indicating that the net increase in the depletion rate for HC_3N (via ion-HC_3N reactions) exceeds that of the formation rate. This pattern is seen for most other polar to strongly polar neutrals in the model with net decreases of a factor of 2–10 in calculated peak and steady state abundances. Polar radicals such as CCH and C_5N which are depleted rapidly via neutral-neutral reactions sometimes show smaller decreases or even increases.

The decreases in the calculated abundances of stable polar molecules are often mirrored by increases in the calculated abundances of protonated ions of these species (e.g., $HCNH^+$, $H_2C_3N^+$) formed from precursor neutrals via rapid reactions with HCO^+ and H_3^+. Thus, use of the large ion-dipole rate coefficients can result in significant increases in the $[XH^+]/[X]$ abundance ratios, where X is a polar neutral, as has already been shown for the case of $[HCS^+]/[CS]$ by Millar *et al.* (1985). These significant increases bring theory and observation much closer to agreement both in the case of $[HCS^+]/[CS]$ (Millar *et al.* 1985) and $[HCNH^+]/[HCN]$ (Ziurys and Turner 1985) and are a strong indication that the rapid ion-polar rate coefficients do occur, at least for the protonation of CS and HCN. It should be noted, however, that there is still disagreement among our calculated value of 4.85×10^{-3} for $[HCS^+]/[CS]$ at steady state; the observationally deduced value of ≥ 0.1 (Irvine, Good, and Schloerb 1983); and the steady state value of 0.088 calculated by Millar *et al.* (1985) who used a small number of reactions. The discrepancy between our calculated value and that of Millar *at al.* (1985) stems from two factors: our use of the reaction between HCS^+ and O (atomic oxygen) and our inclusion of metallic ions such as Mg^+ and Na^+, albeit at a much lower abundance than in models with "high metal" abundances (Leung, Herbst, and

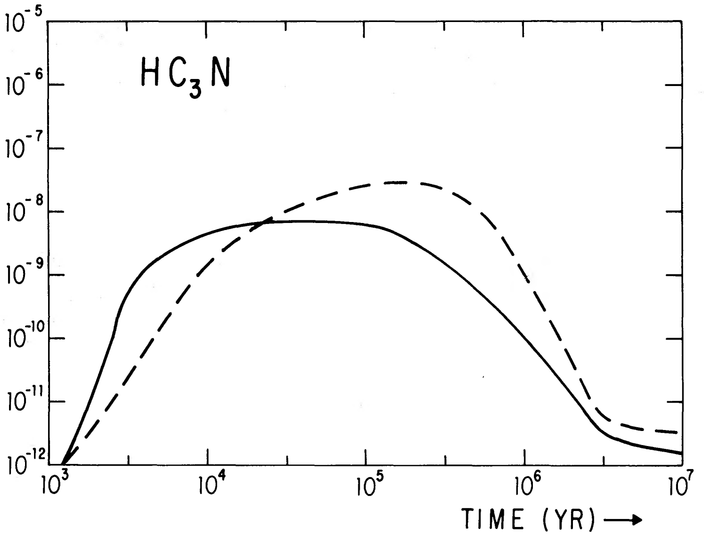

FIG. 1.—Calculated fractional abundances for HC_3N as a function of time for normal ion-molecule rates (*dashed line*) and rapid ion-polar rates (*solid line*)

Huebner 1984; Herbst and Leung 1986). Inclusion of the $HCS^+ + O$ reaction leads to a factor of ~ 5 reduction in the calculated abundance ratio of $[HCS^+]/[CS]$ while inclusion of the metal ions (which results in a higher electron abundance and a more rapid electron recombination rate for HCS^+) reduces this ratio by a factor of ~ 3. Since the calculation of Millar *et al.* (1985) is in much better agreement with observation, it would appear that our "low metal" abundances are still too high (by at least a factor of 3) and that the reaction between HCS^+ and atomic oxygen either occurs more slowly or is less important because the abundance of atomic oxygen is lower than calculated. We have assumed a rate coefficient of 10^{-9} cm^3 s^{-1} for the $HCS^+ + O$ reaction. Other ion-atom reactions involving atomic oxygen have been measured at room temperature to have rate coefficients up to one order of magnitude less than this. The increase in the HCS^+ abundance caused by rapid protonation of CS followed by the rapid $HCS^+ + O$ reaction leads to the increased abundances of some sulfur-containing molecules and atomic sulfur discussed above.

We have also run models with the large ion-polar neutral rate coefficients for a variety of different physical conditions, described in Herbst and Leung (1986), including higher temperature (50 K). Changes induced by the rapid ion-polar rate coefficients in the higher temperature model are less severe because of the $T^{-1/2}$ temperature dependence of the rates given in equations (1) and (2). Since the previous trend in our models has been the enhancement of complex molecular abundances at lower temperatures due to the inverse temperature dependence of radiative association reactions, the use of large ion-dipole rates lessens this effect somewhat. For example, the ratio of the peak abundance of CH_3OH at 10 K to that at 50 K in our previous calculations (Herbst and Leung 1986) is 30. With the assumed large ion-dipole rate coefficients, this ratio drops to 8.

Finally, the overall agreement between model results and observation for dark clouds such as TMC-1 or giant molecular clouds such as OMC-1 is not changed dramatically via inclusion of the larger rates. Indeed, it is now even more the case that calculated abundances of complex molecules are generally too small at steady state. It is still true that these abundances approach observed values at times well before steady state is achieved. In addition, the changes obtained in our model results are significantly smaller than differences between our model results and those of other workers (Millar and Nejad 1985). We are currently including evolutionary effects (Tarafdar *et al.* 1985) in our models and will also investigate the effect of large ion-dipole rates in these calculations.

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