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THE IMPORTANCE OF CLASSES OF NEUTRAL-NEUTRAL REACTIONS IN THE PRODUCTION OF COMPLEX INTERSTELLAR MOLECULES

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ABSTRACT

The role of classes of neutral-neutral reactions in the gas-phase synthesis of complex interstellar molecules is determined via a series of model calculations. Reactions between O or N atoms and bare carbon clusters C_n appear to be critical in hindering the synthesis of complex species. Neutral-neutral reactions involving molecular hydrogen that occur via tunneling under potential energy barriers are shown to aid molecular synthesis. We demonstrate that, despite the existence of rapid neutral-neutral reactions, large abundances of complex molecules can be produced in dense clouds.

Subject headings: ISM: clouds — ISM: molecules — molecular processes

1. INTRODUCTION

Until recently, gas-phase interstellar chemical models of quiescent molecular clouds were able to reproduce the observed abundances of many small and complex species at so-called early times of 10^5–10^6 yr (Herbst & Leung 1989). Current models, however, have difficulty in reproducing the abundances of complex species (Bettens & Brown 1992; Herbst et al. 1994). The cause of this failure is the introduction of many rapid, but highly uncertain, neutral-neutral reactions. It had been assumed in the earlier models that most neutral-neutral reactions do not proceed at significant rates at quiescent cloud temperatures (10 K). Reactions between stable neutral species are undoubtedly slow at low temperature, since such reactions have short-range potential barriers which prohibit their occurrence at low temperatures. There was, however, little evidence for the slowness of neutral reactions in which both of the reactants are radicals, a term usually signifying an "open shell" atom or molecule with a nonsinglet electronic state. Indeed, many oxygen atom-neutral radical reactions are now known to proceed rapidly at room temperature (Baulch et al. 1992). In addition to this exception, Husain (1993), Haider & Husain (1993), and Clary et al. (1994) have investigated rapid room temperature reactions involving neutral carbon atoms and *stable* hydrocarbons. Neutral reactions that are rapid at room temperature may well be rapid at low temperature. Frost, Sharkey, & Smith (1993) have shown that the reaction between stable CO and the OH radical proceeds down to 80 K with a rate coefficient virtually unchanged from its room temperature value. Sims et al. (1992, 1993, 1994a, b) have shown that a variety of reactions between the CN and OH radicals and stable neutral species proceed rapidly at temperatures as low as 13 K and tend to increase in rate as the temperature is lowered from room temperature. In only a few of the above studies have the reaction products been measured.

The inclusion of neutral-neutral reactions into gas-phase chemical models of dense interstellar clouds has occurred gradually. Millar, Leung, & Herbst (1987) realized that a small number of efficient neutral-neutral reactions between atomic oxygen and bare carbon clusters was necessary to avoid an overproduction of complex molecules. Herbst & Leung (1990) included CN-neutral hydrocarbon reactions in their quiescent molecular cloud model and showed that these reactions produce the cyanopolyynes efficiently. With the assumption that long-range permanent quadrupole-permanent dipole forces dominate in reactions between carbon, oxygen, and nitrogen atoms with assorted radicals, Graff (1989) had argued that oxygen atom reactions would be efficient at low temperature, while carbon and nitrogen atom reactions would not. Using this argument as a basis for including a larger number of efficient neutral-neutral reactions in a quiescent cloud interstellar chemical model, Bettens & Brown (1992) found that the production of complex species was seriously curtailed at all times by the large set of oxygen atom-neutral radical reactions.

After Bettens & Brown (1992) published their results, Clary, Stoecklin, & Wickham (1993) and Clary et al. (1994) showed that for carbon atom-hydrocarbon reactions, the dispersion interaction between the two neutral reactants dominates at long-range and is the cause of a large rate coefficient at room temperature and below. With this and the new experimental results in mind, Herbst et al. (1994) incorporated many carbon atom and CN radical-stable neutral reactions, nitrogen atom-radical reactions, and oxygen atom-radical reactions, all at large rates, in their study of the effect of neutral-neutral reactions on dense cloud chemical models. Despite the assumed synthetic nature of the carbon atom-neutral reactions included by Herbst et al. (1994), they obtained abundances of complex species far below the observed values for well-studied dark interstellar clouds such as TMC-1 and L134N.

The analyses of Bettens & Brown (1992) and Herbst et al. (1994) may underestimate the abundances of complex molecules for several reasons. First, Herbst (1994) has suggested that some of the destructive nature of the neutral-neutral reactions could be mitigated by inclusion of so-called hydrogen atom abstraction reactions (HAARs) between hydrocarbon radicals and molecular hydrogen. For example, the radical C_3H produced via the carbon-insertion reaction between C atoms and acetylene could be converted into C_3H_2 via the HAAR

$$C_3H + H_2 \rightarrow C_3H_2 + H \quad (1)$$

which would compete with the destructive reaction between

C_3H and atomic oxygen. Subsequent reactions in which carbon insertion and hydrogenation alternated could produce large hydrocarbons efficiently. Reactions between hydrocarbon radicals and molecular hydrogen need not occur rapidly for such an effect to become important (Herbst 1994) because there is so much H_2 in the interstellar gas. As a test calculation, Herbst (1994) showed that tunneling under short-range potential energy barriers leads to a significant low-temperature rate coefficient for the HAAR between the radical C_2H and H_2.

In addition to the role of HAARs, there is the possibility that, despite the assumption of modelers to the contrary, the $O + C_n$ reactions may not be rapid. The bare carbon clusters considered in interstellar models are sufficiently small that the linear ("straight chain") forms may predominate. Because the linear clusters with n odd possess singlet electronic ground states, their kinetics may resemble that of stable neutral molecules more closely than that of radicals. In addition, even the straight chain clusters with n even, which possess triplet ground electronic states for $n > 2$, are not standard radicals, which typically have an odd number of electrons and lie in doublet ground states.

In this paper, we report the results of a detailed investigation of the sensitivity of complex molecule synthesis to the rates of assorted groups of neutral-neutral reactions. The investigation has been undertaken by running a series of models in which whole sets of such reactions are modified, added, and removed from the reaction network. We have especially tried to determine under what conditions and to what extent the results of previous ion-molecule models in producing large abundances of complex molecules can be reproduced. We have not concerned ourselves with concentrations of individual species, but rather with the overall production of complex molecules. Somewhat arbitrarily, we have chosen as complex species the following 11 molecules: C_nH, $n = 2$–6; C_nH_2, $n = 3$–4; $HC_{2n+1}N$, $n = 1$–4, all of which have been detected in TMC-1. Two criteria have been utilized to determine the complex molecule production efficiency. The first is given by $N_{\rm agree}/N_{\rm tot}$, where $N_{\rm agree}$ is the number of complex species which agree with the observed abundance in TMC-1 within an order or magnitude at any given time and $N_{\rm tot}$ is the total number of complex species being compared with observation, which in this case is 11. Our second measure of overall agreement with observation is less strict. It is given by $N_>/N_{\rm tot}$, where $N_>$ is the number of complex species with abundance calculated to be greater than 1/10 of the observed abundance in TMC-1. The purpose of the latter criterion is to determine whether or not enough complex species can be produced at any given time; in developing this criterion we have not been as concerned about overproducing complex species. The overproduction of gas-phase complex species can be reduced, depending on the time, by considering grain adsorption, or by changing poorly determined physical conditions and parameters.

In the next section of this paper we describe the changes made to the reaction network of Herbst & Leung (1989, 1990) to obtain the various models used in this work. This is followed by a presentation of our results and a discussion of them.

2. REACTION SETS

We refer to the gas-phase dense cloud model of Herbst & Leung (1989), which does not include any of the rapid neutral-neutral reactions considered more recently, as the old standard model. This model has been updated to include many new reactions, 133 new species, and two new elements—chlorine and phosphorus. The new species added to the old standard model are listed in Table 1. The new reactions include organo-sulfur chemistry (Millar & Herbst 1990) and cosmic-ray induced photodestruction (Gredel et al. 1989). The current model, referred to as the new standard model, contains 3785 gas-phase reactions involving 409 species. It resembles the UMIST network (Farquhar & Millar 1993) but contains a more thorough treatment of complex molecules and uses dipole-enhanced rates for ion-molecule reactions.

The model described in the work of Herbst et al. (1994), where the role of an assortment of rapid neutral-neutral reactions has been considered, is referred to here as the old neutral-neutral model. A new neutral-neutral model has been developed by adding rapid neutral-neutral reactions to the new standard model. In developing the new neutral-neutral model, we have reconsidered the neutral-neutral reactions added/revised by Herbst et al. (1994), and have included additional neutral-neutral reactions for consistency as well as revising and deleting some rate coefficients. These changes are listed in Table 2, where reaction rate coefficients are tabulated in the form $A \times [T(\mathrm{K})/300]^B$ with A in units of $\mathrm{cm^3\ s^{-1}}$. We have concentrated on reactions involving atomic C, N, and O because these neutral species are the most abundant reactive neutrals present in these gas-phase models. Given the lack of experimental and ab initio theoretical data on low-temperature neutral-neutral reactions, we have used exothermicity and spin conservation, where known, as a guide in deciding upon which reactions may proceed and what products may be produced. These two criteria are by no means very selective, so we have also used a set of guiding principles for determining which neutral-neutral reactions may proceed at significant rates.

Based upon the reported rapid room temperature reactions between C and stable hydrocarbons (Husain 1993; Haider & Husain 1993; Clary et al. 1994) we have considered that all other C-hydrocarbon reactions are rapid and proceed with a rate coefficient of $2 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$. The rapidity of the C atom-hydrocarbon reactions is unusual, so without evidence that C reacts rapidly with the N-containing or O-containing species we assume that C reacts rapidly *only* with the radicals of these two groups of chemical species.

Upon reference to Baulch et al. (1992), it is seen that O reacts rapidly, with no detectable barrier, with the species CH, $^3CH_2$, CH_3, CHO, CH_3O, CN, C_2H, C_2H_3, C_2H_5, and CHCO at temperatures ≥ 300 K. Barriers or small rate coefficients are observed for the reactants CH_4, HCHO, CH_3COOH, C_2H_2, C_2H_4, C_2H_6, CH_2CO, CH_3CHO, and C_2H_5OOH, all of which are "stable" (closed shell, singlet) molecules. Extrapolating the room temperature results, we assume that O reacts rapidly *only* with radicals at ~ 10 K. We have assumed a rate coefficient of $1 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$ for all O atom-neutral radical reactions based on the measured rate for the reaction between O and C_2H_5, which is the fastest reaction in this class. Few data are available for N atom-neutral reactions, but N has been observed to react rapidly with the radicals CN (Baulch et al. 1992) and CH_3 (Stief et al. 1988; Marston et al. 1989; Marston, Nesbitt, & Stief 1989). We again assume, as in the case of the O atom-neutral radical reactions, that *only* radicals react with N atoms with a rate coefficient of $1 \times 10^{-10}\ \mathrm{cm^3\ s^{-1}}$.

The new neutral-neutral model is slightly less efficient in the formation of complex species than the old neutral-neutral model, because several extra processes were added that had

TABLE 1

NEW SPECIES INCLUDED IN NEW STANDARD MODEL

One-Carbon						
HCSi	HCP	HCS	H_2CN	NH_2CN	$SiCH_2$	$SiCH_3$
CH_2PH	SiNC	CP	CCl			
HNC^+	$HNCO^+$	$SiNCH^+$	HCP^+	H_2NC^+	PCH_2^+	H_2CCl^+
NH_2CNH^+	$SiCH_3^+$	PCH_3^+	$SiCH_4^+$	PCH_4^+	NCO^+	$SiNC^+$
CP^+	CCl^+					
Two-Carbon						
SiC_2H	HCCP	SiC_2H_2	$HCOOCH_3$	C_2H_5		
CCO	SiC_2	CCP	C_2S			
SiC_2H^+	PC_2H^+	HC_2S^+	$SiC_2H_2^+$	$PC_2H_2^+$	$SiC_2H_3^+$	$PC_2H_3^+$
$COOCH_4^+$	$PC_2H_4^+$	$H_5C_2O_2^+$	$C_2H_6^+$	CNC^+	$C_2N_2^+$	C_2O^+
SiC_2^+	CCP^+	C_2S^+				
Three-Carbon						
SiC_3H	C_2H_6CO	SiC_3	C_3P	C_3S		
SiC_3H^+	PC_3H^+	HC_3S^+	$SiC_3H_2^+$	$C_2H_6CO^+$	$C_3H_6OH^+$	C_3O^+
SiC_3^+	C_3S^+					
Four-Carbon						
SiC_4	C_4P	C_4S				
HC_4N^+	SiC_4H^+	PC_4H^+	HC_4S^+	$H_2C_4N^+$	$PC_4H_2^+$	$H_3C_4N^+$
SiC_4^+	C_4P^+	C_4S^+				
Nitrogen						
NO_2	SiN	HNSi	PN	N_2O		
SiN^+	$HNSi^+$	$SiNH_2^+$	PN^+	HPN^+	PNH_2^+	PNH_3^+
Oxygen						
H_2SiO	PO	HPO	ClO	O_2H	H_2O_2	SiO_2
H_2SiO^+	H_3SiO^+	PO^+	HPO^+	H_2PO^+	ClO^+	$HSiO_2^+$
SO_2^+	HSO_2^+					
Assorted						
SiH_2	SiH_3	SiH_4	SiH_3^+	SiH_4^+	SiH_5^+	
P	PH	PH_2	P^+	PH^+	PH_2^+	PH_3^+
S_2	HS_2	H_2S_2	S_2^+	S_2H^+	$H_2S_2^+$	$H_3S_2^+$
Cl	HCl	Cl^+	HCl^+	H_2Cl^+		

been overlooked in the earlier approach and the rate coefficients for many oxygen atom-radical neutral reactions were revised upward by a factor of 2.

2.1. *Models 1–6*

In order to determine the effects of various groups of neutral-neutral reactions on the abundances of complex species we have run variations of the above chemical models, summarized as models 1–6 in Figure 1. Reaction sets for all models in this paper are available from the authors. In model 1, we have removed the reactions

$$O + C_n \rightarrow C_{n-1} + CO \, , \qquad (2)$$

where $n = 2$–9, from the new standard model. The purpose of running model 1 was to determine the negative influence of O-carbon cluster reactions. In model 2 we modified the new standard model by enlarging the common rate coefficient for reaction (2) from $k = 5 \times 10^{-11}(T/300)^{1/2}$ cm^3 s^{-1} to 1×10^{-10} cm^3 s^{-1}, the standard rate in the new neutral-neutral model, and further adding the reactions

$$N + C_n \rightarrow C_{n-1} + CN \, , \qquad (3)$$

where $n = 2$–9, with the same rate coefficient as reactions (2).

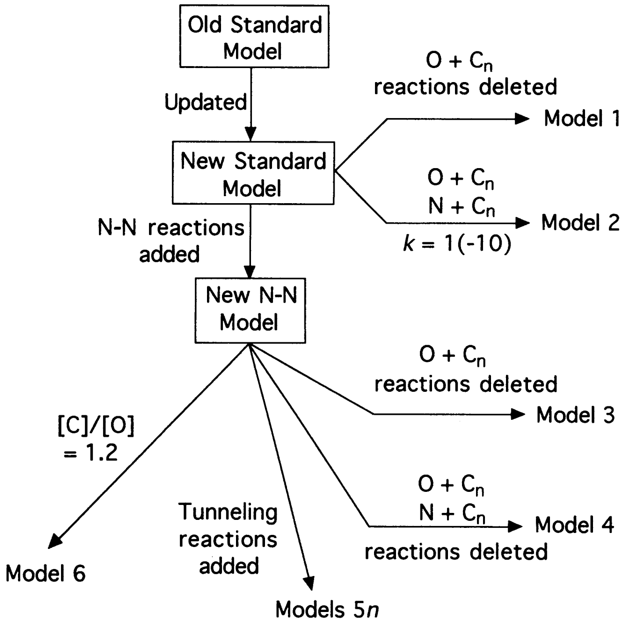

FIG. 1.—Distinguishing features of models

TABLE 2

CHANGES IN RAPID NEUTRAL-NEUTRAL REACTION SET

Reactant 1	Reactant 2	Product 1	Product 2		A	B
Revisions						
O	C2	CO	C		1.0E-10	0.0
O	C2H	CO	CH		1.0E-10	0.0 [1]
O	C3	CO	C2		1.0E-10	0.0
O	C4	CO	C3		1.0E-10	0.0
O	C4H	C3H	CO		1.0E-10	0.0
O	C5	CO	C4		1.0E-10	0.0
O	C5H	CO	C4H		1.0E-10	0.0
O	C6	CO	C5		1.0E-10	0.0
O	C6H	CO	C5H		1.0E-10	0.0
O	C7	CO	C6		1.0E-10	0.0
O	C7H	CO	C6H		1.0E-10	0.0
O	C8	CO	C7		1.0E-10	0.0
O	C8H	CO	C7H		1.0E-10	0.0
O	C9	CO	C8		1.0E-10	0.0
O	C9H	CO	C8H		1.0E-10	0.0
O	C2H3	CO	CH3		3.3E-11	0.0[1]
O	C2H3	OH	C2H2		3.3E-11	0.0[1]
O	C3H3	CO	C2H3		3.3E-11	0.0
O	C3H3	OH	C3H2		3.3E-11	0.0
O	HCO	OH	CO		5.0E-11	0.0
O	HCO	H	CO2		5.0E-11	0.0
O	C2N	CO	CN		5.0E-11	0.0
O	C3N	CO	C2N		5.0E-11	0.0
O	C3O	C3	O2		5.0E-11	0.0
O	C4N	C3N	CO		5.0E-11	0.0
O	C5N	C4N	CO		5.0E-11	0.0
N	C2	CN	C		1.0E-10	0.0
N	C4N	CN	C3N		5.0E-11	0.0
N	C4N	C4	N2		5.0E-11	0.0
CN	NH3	NH2	HCN		1.3E-11	-1.1[2]
Additions						
O	C2N	NO	C2		5.0E-11	0.0
O	C3N	NO	C3		5.0E-11	0.0
O	C3O	CO	CCO		5.0E-11	0.0
O	C4N	NO	C4		5.0E-11	0.0
O	C5N	NO	C5		5.0E-11	0.0
O	C7N	NO	C7		1.0E-10	0.0
O	C9N	NO	C9		1.0E-10	0.0
O	CCO	C2	O2		5.0E-11	0.0
O	C2H3	HCO	CH2		3.3E-11	0.0
O	C2H5	H2CO	CH3		9.2E-11	0.0[1]
O	C2H5	C2H4O	H		1.8E-11	0.0[1]
O	C3H3	HCO	C2H2		3.3E-11	0.0
O	C2H2N	CO	H2CN		1.0E-10	0.0
C	CCO	C2	CO		2.0E-10	0.0
C	C3	C4			1.0E-10	0.0
C	C3O	C3	CO		2.0E-10	0.0
C	HCO	CH	CO		2.0E-10	0.0
C	C2H5	C3H4	H		2.0E-10	0.0
C	C3H4	C4H2	H	H	1.0E-10	0.0
C	C3H4	C3H	CH3		1.0E-10	0.0
C	CH3C4H	C6H2	H	H	1.0E-10	0.0
C	CH3C4H	C5H	CH3		1.0E-10	0.0
C	CH3C6H	C8H2	H	H	1.0E-10	0.0
C	CH3C6H	C7H	CH3		1.0E-10	0.0
C	C9H	C7H	C3		2.0E-10	0.0
C	C9H2	C8H	C2H		2.0E-10	0.0
C	C2N	CN	C2		2.0E-10	0.0
C	C3N	CN	C3		2.0E-10	0.0
C	C4N	CN	C4		2.0E-10	0.0

TABLE 2—*Continued*

Reactant 1	Reactant 2	Product 1	Product 2		A	B
C	C5N	CN	C5		2.0E-10	0.0
C	C7N	CN	C7		2.0E-10	0.0
C	C9N	CN	C9		2.0E-10	0.0
C	C2H2N	HC3N	H		2.0E-10	0.0
N	C3	CN	C2		1.0E-10	0.0
N	C4	CN	C3		1.0E-10	0.0
N	C5	CN	C4		1.0E-10	0.0
N	C6	CN	C5		1.0E-10	0.0
N	C7	CN	C6		1.0E-10	0.0
N	C8	CN	C7		1.0E-10	0.0
N	C9	CN	C8		1.0E-10	0.0
N	C6H	C5H	CN		1.0E-10	0.0
N	C8H	C7H	CN		1.0E-10	0.0
N	C2H3	CN	CH3		1.0E-10	0.0
N	C2H5	C2H3N	H	H	1.0E-10	0.0
N	C7N	C5N	C2N		1.0E-10	0.0
N	C9N	C7N	C2N		1.0E-10	0.0
N	CCO	C2	NO		1.0E-10	0.0
N	H2CN	NH	HCN		1.0E-10	0.0
N	C2H2N	H2CN	CN		1.0E-10	0.0
CN	NH3	NH2CN	H		1.3E-11	-1.1[2]
C2H	O2	CO	HCO		3.0E-11	0.0[3]
		Deletions				
C	HC3N	C4N	H		2.0E-10	0.0
O	C7N	OCN	C6		2.0E-11	0.5
O	C9N	OCN	C8		2.0E-11	0.5

NOTE.—The rate coefficients are listed as $A \times [T(\mathrm{K})/300]^B$, where A is in units of $\mathrm{cm^3\ s^{-1}}$.

REFERENCES.—(1) Products from Baulch et al. 1992; (2) Two sets of products have now been assumed; the rate has been measured by Sims et al. 1994a; (3) rate and products from Baulch et al. 1992.

The results of model 2 will indicate to what extent the faster O-carbon cluster and N-carbon cluster reactions influence the buildup of complex species compared with the new standard model. Model 3, which is analogous to model 1, is a revision of the new neutral-neutral model in which we have removed reactions (2). In model 4 we have also removed reactions (3) from the new neutral-neutral model. These two models will be used to establish whether or not the O- and N-carbon cluster reactions have any impact on the new neutral-neutral model.

As indicated in Figure 1, we have added HAARs to the new neutral-neutral model to obtain models 5*n*. The HAARs are of the types

$$C_n + H_2 \rightarrow C_nH + H \,, \qquad (4)$$

where $n = 2, 4, 6$–9,

$$C_nH + H_2 \rightarrow HC_nH + H \,, \qquad (5)$$

where $n = 2, 4, 6, 8$, and

$$C_{2n+1}N + H_2 \rightarrow HC_{2n+1}N + H \,, \qquad (6)$$

where $n = 0$–4. The values of n utilized refer to reactions known or calculated to be exothermic. (Note that reaction [1] has been shown to be endothermic—see below). The products in reactions (5) are known as polyacetylenes. Although we had expected the most reasonable exothermic products for reactions (5) with n odd to be carbenes (H_2C_n) ab initio calculations, discussed below, show that these reactions are endothermic. We have not considered cyclic products for reactions (5) even though they might be exothermic because of the high probability of large potential energy barriers.

To determine whether or not the various feasible reactions (5) are exothermic or endothermic, it was necessary to determine the heats of formation of the carbenes H_2C_{2n+1}, $n = 1$–4. The heats of formation of the polyacetylenes are already known (Lias et al. 1988), but we have calculated them here as a check of our method. We used an approximate procedure known as the isodesmic bond separation method (Hehre et al. 1986). The level of ab initio theory used was the MP2/6-31G*. Calculations were performed with the GAUSSIAN 92 suite of programs (Frisch et al. 1992). Geometry optimizations were performed on the carbenes and polyacetylenes with the symmetry constraints of C_{2v} and $D_{\infty h}$, respectively. Listed in Table 3 are the calculated heats of formation at 298 K for the carbenes and polyacetylenes. For the polyacetylenes we have included the experimental values to show the reliability of the isodesmic approach.

TABLE 3

CALCULATED AND EXPERIMENTAL HEATS OF FORMATION ($\mathrm{kJ\ mol^{-1}}$ [a]) FOR THE C_nH_2 (SINGLET) SPECIES AT 298 K

Species	Symmetry	ΔH_f^0(calc.)	ΔH_f^0(exp.)[b]
H_2C_3..........	C_{2v}	512	...
HC_4H.........	$D_{\infty h}$	443	440
H_2C_5..........	C_{2v}	723	...
HC_6H.........	$D_{\infty h}$	652	652
H_2C_7..........	C_{2v}	933	...
HC_8H.........	$D_{\infty h}$	856	864
H_2C_9..........	C_{2v}	1142	...

[a] $1\ \mathrm{kJ\ mol^{-1}} = 120.27$ K.

[b] Experimental values taken from Lias et al. 1988.

The HAAR reactions in models 5*n* have been added to test the assertion of Herbst (1994) that they aid in the synthesis of complex molecules. Given the likely existence of short-range potential energy barriers, they most probably occur only via tunneling. A wealth of experimental and theoretical evidence shows that the analogous ion-molecule HAAR:

$$NH_3^+ + H_2 \rightarrow NH_4^+ + H \quad (7)$$

proceeds at low temperature with a rate approaching 10^{-12} cm^3 s^{-1} by tunneling under a small potential barrier (Luine & Dunn 1985; Herbst et al. 1991) and there is some evidence that the analogous ion-molecule HAAR involving the hydrocarbon ion $C_2H_2^+$ proceeds likewise (Yamashita & Herbst 1992).

The same rate coefficient was used for each of the tunneling HAARs given in reactions (4)–(6). This rate coefficient was chosen to be 1.0×10^{-15}, 1.0×10^{-14}, 3.2×10^{-14}, and 1.0×10^{-13} cm^3 s^{-1} in models 5*a*–5*d*, respectively, corresponding approximately to $1/10^5$ $1/10^4$, 1/3000, and 1/1000 of the collision rate. The (uncertain) rate calculated by Herbst (1994) for the reaction between the radical C_2H and H_2 at 10 K is 2.2×10^{-15} cm^3 s^{-1}.

Finally, in model 6, we have reduced the elemental abundance of oxygen in the new neutral-neutral model from that used in standard oxygen-rich models (e.g., Herbst & Leung 1989) such that [C]/[O] = 1.2. Carbon-rich gas-phase models are known to produce large abundances of complex molecules in standard models at all times from early time to steady state, but their synthetic power in the presence of rapid neutral-neutral reactions is unknown.

All model calculations have been run with low-metal abundances under constant physical conditions assumed to represent dark or quiescent dense clouds, viz., large A_v (>10), $T = 10$ K, and $[H] + 2[H_2] = 2 \times 10^4$ cm^{-3}. Initial abundances are as discussed in Herbst & Leung (1989) except for the carbon-rich model. The elemental abundances of chlorine and phosphorus are taken from the UMIST file (Farquhar & Miller 1993). As in previous models with constant physical conditions, the abundances of most complex molecules in oxygen-rich models go through peaks at so-called early times of 10^{5-6} yr before declining. Steady-state abundances are reached in 10^{7-8} yr.

3. RESULTS

The results of the above models have been used to derive the flow diagram given in Figure 2, which shows whether or not sufficient abundances of complex molecules are produced at some period of time. This figure is to be read in the following way. First, if [C] > [O], then we are able to produce large amounts of complex species. If this condition is not met, which is the assumed case in virtually all models of dense clouds, but if N and O do not react efficiently with neutral carbon clusters, we are also able to produce enough complex species. In addition, if these reactions are efficient but the remaining rapid neutral-neutral reactions added to the new standard model to produce the new neutral-neutral model, e.g., the O–C_nH radical reactions and the C-hydrocarbon reactions, are not efficient, then we are again able to produce sufficient abundances of complex molecules. Even if these remaining neutral-neutral reactions are efficient, then we can still invoke "rapid" tunneling HAARs in order to produce enough complex species. However, if the HAAR reactions are too slow and the above criteria for forming complex species are not met, then we can conclude only that low-temperature gas-phase chemistry cannot explain the abundances of complex molecules with our present understanding of the chemistry and elemental abundances. In the following paragraphs we give evidence for the above conclusions in the form of figures which contain plots of both $N_{\rm agree}/N_{\rm tot}$ and $N_>/N_{\rm tot}$ (defined in the introduction) versus time for assorted models. If the two plots are similar or identical for a given model, then it is clear that few if any species are being overproduced. If, on the other hand, the plot of $N_>/N_{\rm tot}$ lies at unity for a significant period of time while that of $N_{\rm agree}/N_{\rm tot}$ lies well below unity for the same period, it is clear that many molecules are being overproduced.

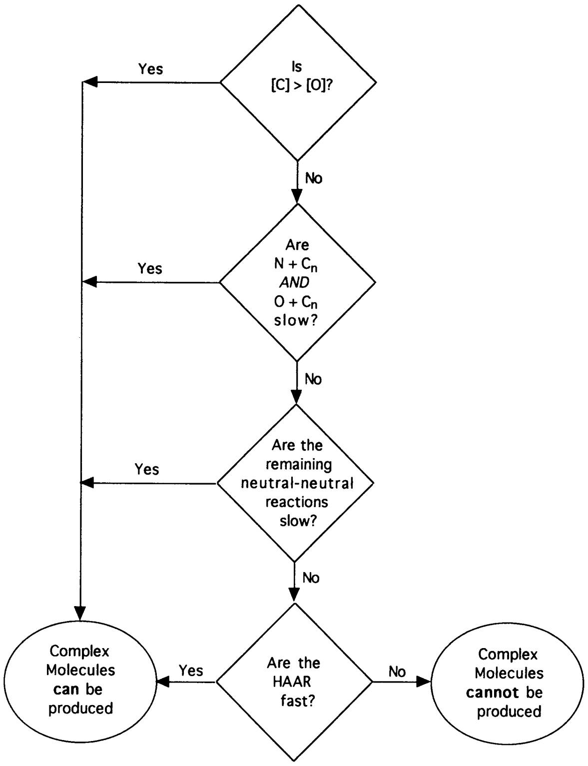

FIG. 2.—Flow diagram summarizing the efficiency of the assorted models in producing complex molecules.

In Figure 3, the results for $N_{\rm agree}/N_{\rm tot}$ (Fig. 3*a*) and $N_>/N_{\rm tot}$ (Fig. 3*b*) are plotted versus time for the new standard model, model 1, and model 2. The first point to note from these figures is that the complex species are overproduced in all models between 10^4 yr and $10^{5.5}$ yr. Second, we note that with the O-neutral carbon cluster reactions removed (model 1) we push the time of best agreement up to 10^6 yr and extend the period in which complex species are efficiently produced. These results are similar to those obtained earlier by Millar et al. (1987). Third, we can see by the similarity between the new standard model and model 2 that the inclusion of N-neutral carbon cluster reactions and the larger rate for O-neutral carbon cluster reactions have little impact. This is partially due to the lower relative abundance of N compared with O and the fact that at early times complex species are produced very efficiently so that the faster O atom-neutral carbon cluster reactions do not lower the abundances of any of the 11 complex species below 1/10 of the observed values. Thus we find in model 2 a satisfactory model for producing complex species in quiescent clouds at early times even if the O *and* N-neutral carbon cluster reactions are efficient.

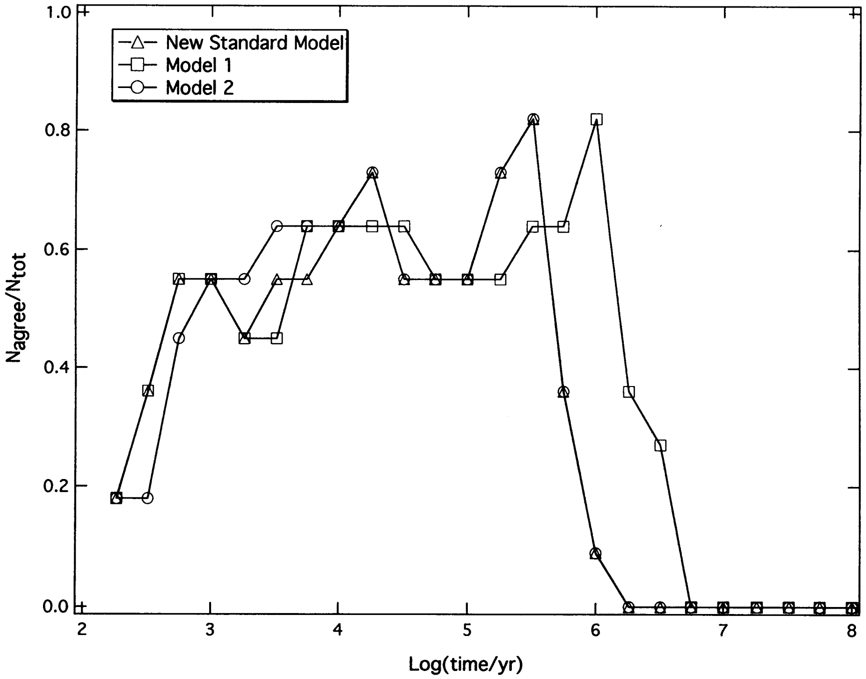

FIG. 3*a*

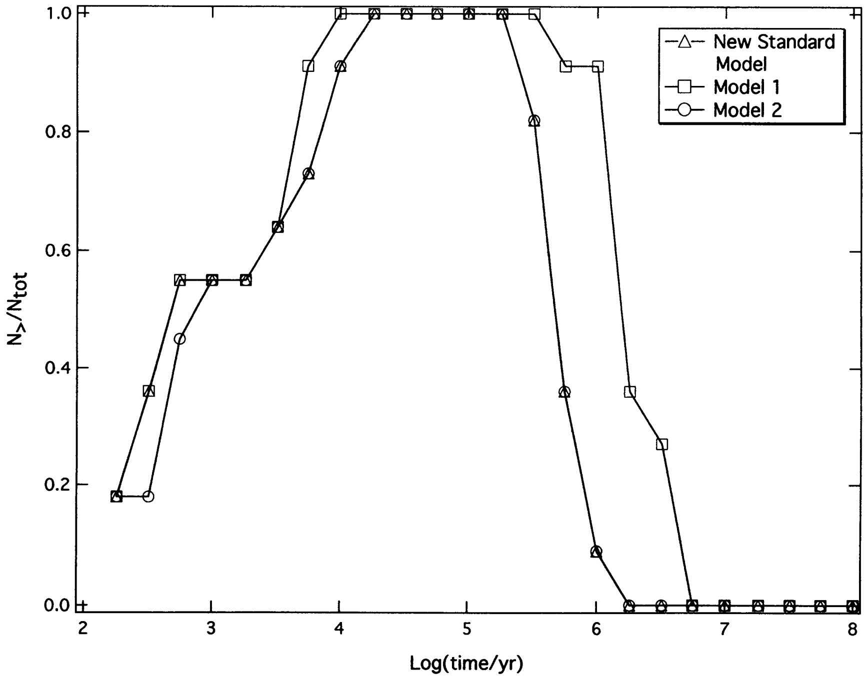

FIG. 3*b*

FIG. 3.—(*a*) The fraction of complex molecules in order-of-magnitude agreement with observation in TMC-1 is plotted vs. time. The models considered are the new standard model, model 1, and model 2. (*b*) The fraction of complex molecules calculated to have at least 1/10 of the observed abundance in TMC-1 is plotted vs. time for the same models as in (*a*).

The results of the new neutral-neutral model and models 3 and 4 are presented in Figures 4*a* and *b*, which show N_{agree}/N_{tot} and $N_{>}/N_{tot}$ versus time, respectively. These figures indicate the destructive nature of the neutral-neutral reactions upon the complex species. It can be seen that the removal of the O-neutral carbon cluster reactions has little impact on the results, mainly because the N-neutral carbon cluster reactions still proceed (model 3). However, with their removal as well from the reaction set (model 4) the production of complex species becomes efficient once more. The overproduction of complex species observed in Figure 3 is no longer present, so that some of the efficiency for building up the complex species is lost in

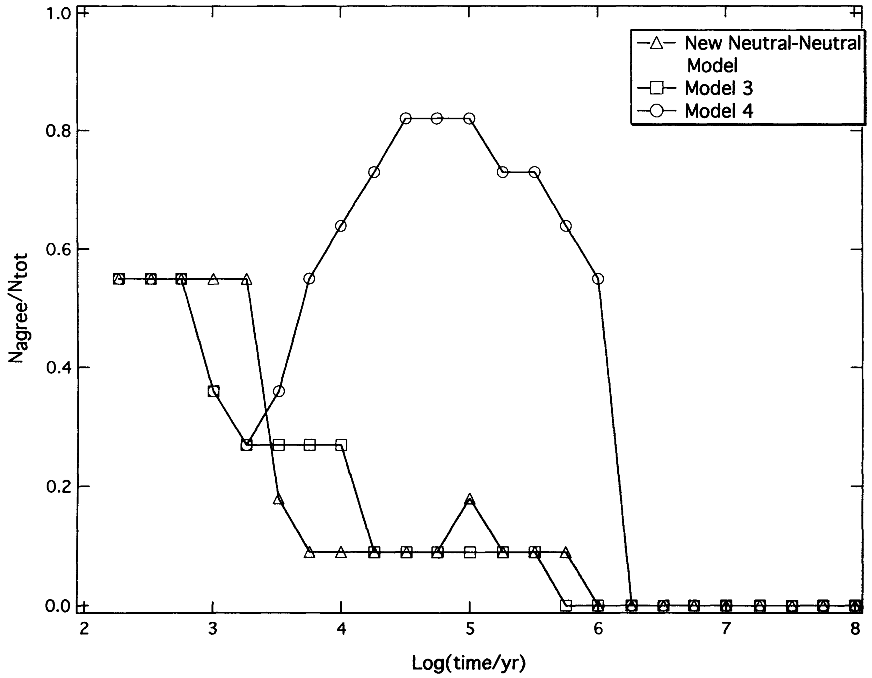

FIG. 4*a*

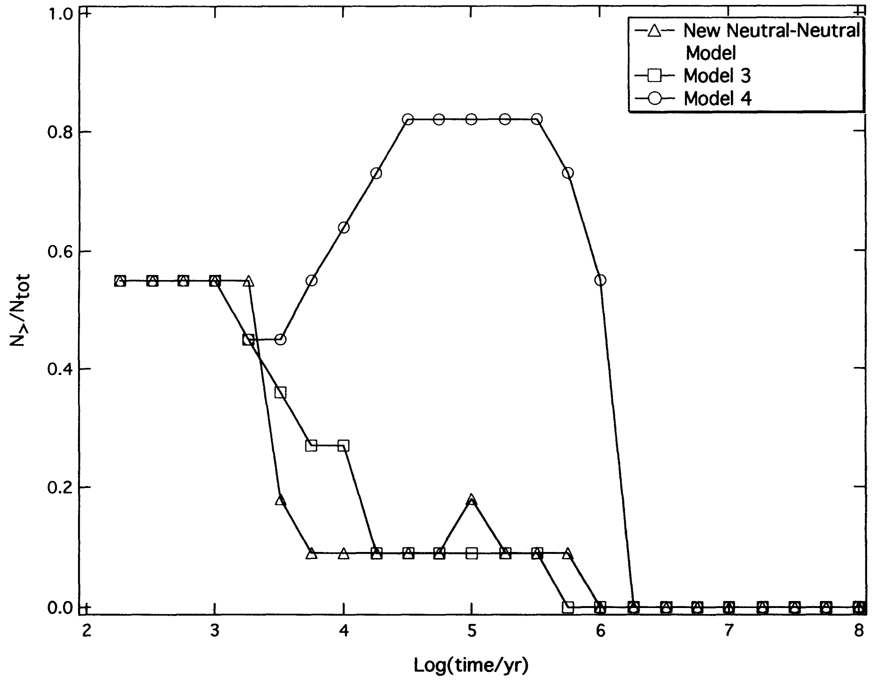

FIG. 4*b*

FIG. 4.—(*a*) The fraction of complex molecules in order-of-magnitude agreement with observation in TMC-1 is plotted vs. time. The models considered are the new neutral-neutral model, model 3, and model 4. (*b*) The fraction of complex molecules calculated to have at least 1/10 of the observed abundance in TMC-1 is plotted vs. time for the same models as in (*a*).

model 4. Nevertheless, Figure 4 shows that with the removal of *both* O and N-neutral carbon cluster reactions, complex species can be efficiently produced even though many other neutral-neutral reactions are rapid. In addition, the clusters are predicted to have large abundances and to play a major role in synthesis through association reactions with carbon ions (Suzuki 1983; Brown, Cragg, & Bettens 1990). We have also run models where we have removed the O and N atom-singlet cluster reactions from the new neutral-neutral model. We found that the results were intermediate between the new neutral-neutral model and model 4. Thus the efficiency of complex species formation was improved, but not enough to

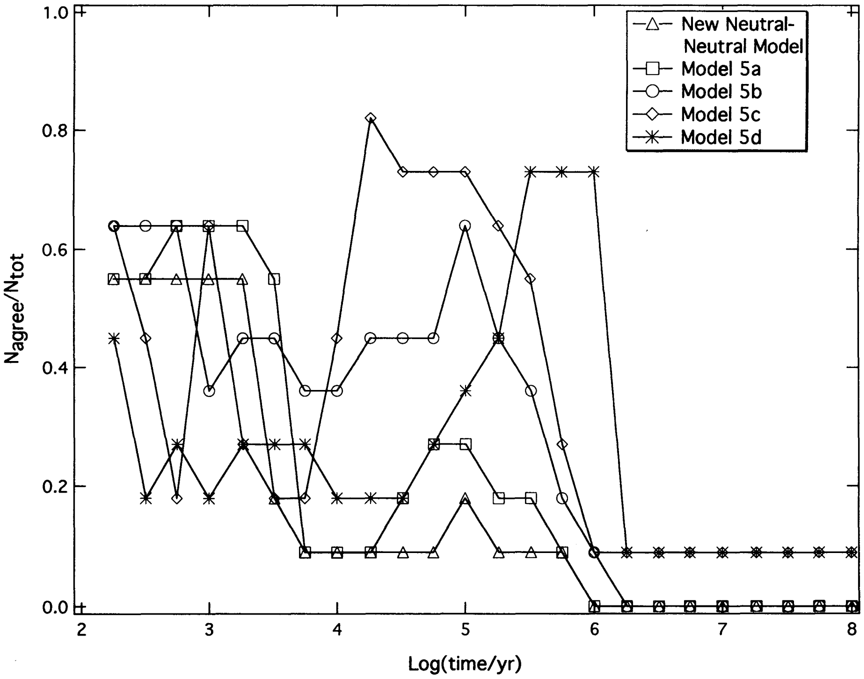

FIG. 5*a*

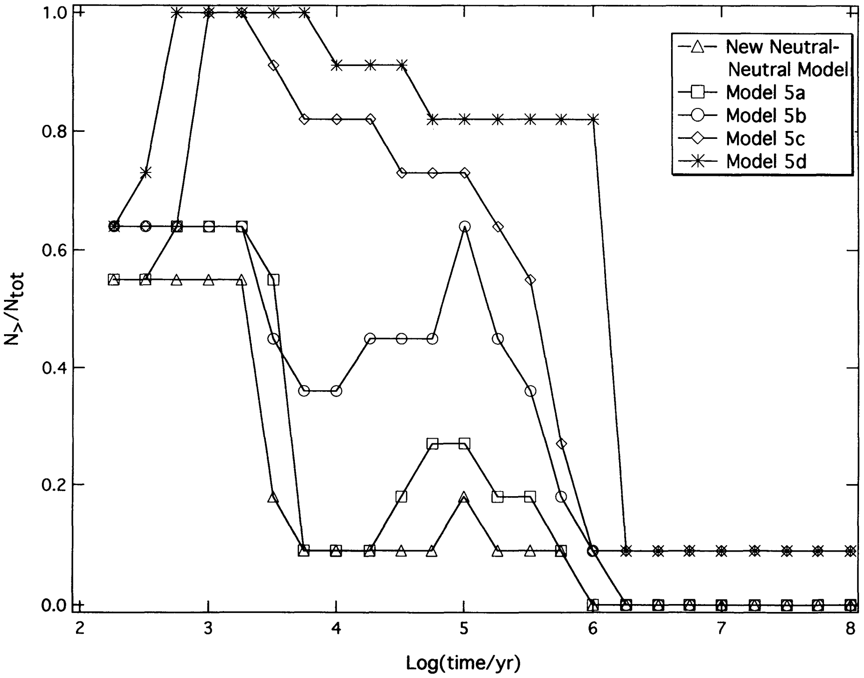

FIG. 5*b*

FIG. 5.—(*a*) The fraction of complex molecules in order-of-magnitude agreement with observation in TMC-1 is plotted vs. time. The models considered are the new neutral-neutral model, and models 5*a*–5*d*, which contain HAARs with varying rates. (*b*) The fraction of complex molecules calculated to have at least 1/10 of the observed abundance in TMC-1 is plotted vs. time for the same models as in (*a*).

satisfactorily reproduce the observed abundances of these species.

Shown in Figures 5*a* and 5*b* are the results of the new neutral-neutral model and models 5*a*–5*d* for N_{agree}/N_{tot} and $N_>/N_{tot}$ versus time, respectively. It can be seen that for model 5*a*, where the tunneling HAARs have rate coefficients of 1.0×10^{-15} cm^3 s^{-1}, there is little difference from the new neutral-neutral model. However, Figure 5*b* shows a systematic increase in the efficiency of building complex species as the HAAR rate coefficients are increased, as suggested by Herbst (1994). In fact, the models with tunneling HAARs are able to produce the complex species efficiently when the rate coeffi-

TABLE 4

FRACTIONAL ABUNDANCES (X/H_2) FOR MODELS COMPARED WITH TMC-1

Molecule	TMC-1	N S	N N-N	Model 4	Model 5*c*
C_2H........	5 (−08)	2.6 (−08)	1.4 (−09)	2.5 (−09)	3.1 (−09)
C_3H........	5 (−10)	1.8 (−08)	2.6 (−09)	2.8 (−09)	5.5 (−09)
C_4H........	2 (−08)	4.2 (−09)	5.7 (−10)	4.7 (−10)	2.2 (−09)
C_5H........	3 (−10)	1.2 (−09)	2.7 (−11)	2.6 (−10)	1.9 (−09)
C_6H........	1 (−10)	6.9 (−10)	6.9 (−12)	1.4 (−10)	6.1 (−10)
C_3H_2.......	1 (−08)	1.1 (−08)	1.0 (−09)	1.4 (−08)	7.8 (−10)
C_4H_2.......	8 (−10)	1.1 (−08)	2.2 (−11)	4.8 (−09)	4.9 (−09)
HC_3N......	6 (−09)	6.4 (−08)	3.2 (−10)	2.3 (−09)	3.1 (−08)
HC_5N......	3 (−09)	4.0 (−09)	7.9 (−11)	4.5 (−10)	2.4 (−08)
HC_7N......	1 (−09)	4.9 (−10)	1.8 (−12)	1.9 (−10)	7.5 (−09)
HC_9N......	3 (−10)	4.8 (−11)	8.2 (−14)	7.6 (−11)	1.4 (−09)

NOTE.—$a(-b)$ refers to $a \times 10^{-b}$. The abbreviations NS and N N-N refer to the new standard and new neutral-neutral models, respectively. The times chosen are approximately 10^5 yr except for model 5*c*, for which a time of approximately 2×10^4 yr has been chosen. The observed fractional abundances for TMC-1 are taken from Ohishi, Irvine, & Kaifu 1992.

cients are $\geq 3.2 \times 10^{-14}$ cm^3 s^{-1} (models 5*c*–5*d*). If one looks at the time dependence in Models 5*c* and 5*d*, one sees a very rapid early build up of complex species leading to an overproduction of these species (compare Fig. 5*a* and 5*b*). After this initial rapid buildup, the abundance of the complex species drops very slowly, such that the greater the buildup, the longer it takes for the concentrations to drop and reach steady state.

In Table 4, we present fractional abundances for the 11 complex molecules utilized in this paper obtained from the following models at the most propitious early times: new standard model, model 4, model 5*c*, and the new neutral-neutral model. The results are compared with observed fractional abundances in TMC-1. Of the four models, only the new neutral-neutral model clearly fails to reproduce the complex molecule abundances. Detailed results for all models are available from the authors.

Finally, in Figure 6 we give the results of the carbon-rich model, model 6. As is evident, we are easily able to produce complex species, as shown by the $N_>/N_{tot}$ curve. Specifically, at and after $10^{5.5}$ yr, all 11 complex species can be formed in sufficient abundance, and approximately 40% are overproduced.

4. DISCUSSION

The O- and N-neutral carbon cluster reactions appear to play a crucial role in the formation of complex species in oxygen-rich models. If these reactions are slow at 10 K, then we are able to produce significant amounts of complex species even if the remaining neutral-neutral reactions are efficient (see model 4 results in Fig. 4, Table 4). Experimental or high-quality theoretical calculations are required to study these reactions, which are especially uncertain in rate because of the poorly understood chemical nature of the straight chain carbon clusters. If both the atom-carbon cluster reactions and the other neutral-neutral reactions are rapid at low temperature, then we require that the tunneling HAARs also be efficient (models 5*c*, 5*d*) if we are to form significant amounts of complex species. The condition for failure of oxygen-rich models to produce sufficient abundances of complex molecules to explain observations in TMC-1 or even other (less fecund) quiescent sources is that all classes of neutral-neutral reactions in the model be rapid at low temperatures and that tunneling HAARs be inefficient. Of course, if [C] > [O], then regardless of whether neutral-neutral reactions are fast we can easily form nonoxygen containing complex molecules in copious amounts. This latter point is of interest and warrants further discussion.

It has long been known that CO is a reservoir species for C and O, but for oxygen-rich models there still remain significant

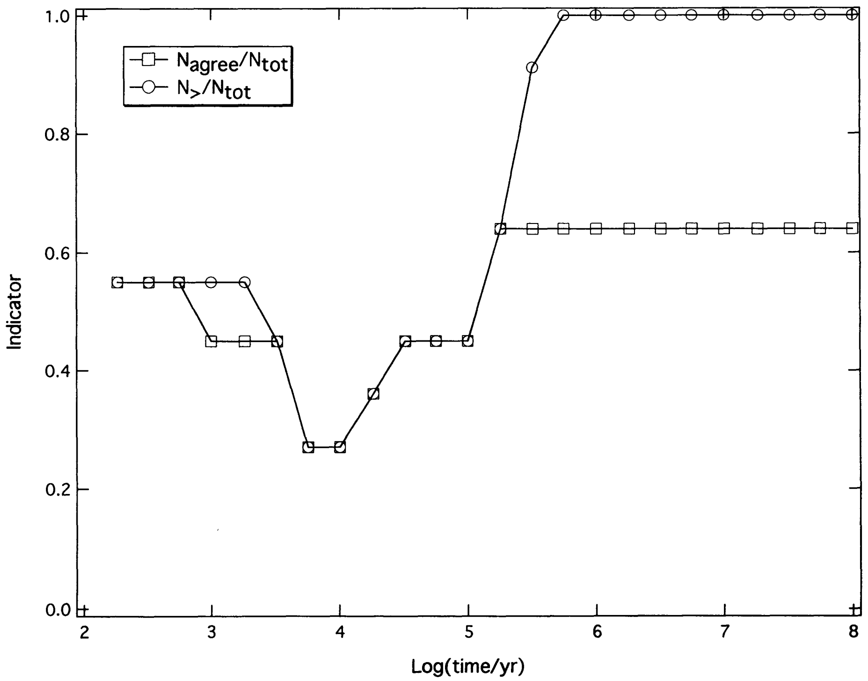

FIG. 6.—Two indicators of the molecular production efficiency of the new neutral-neutral model with a carbon-to-oxygen elemental ratio of 1.2 are plotted vs. time. The indicators are the fraction of complex molecules calculated to be within an order of magnitude of their observed abundances in TMC-1, and the fraction of complex molecules calculated to have at least 1/10 of their observed abundances in TMC-1.

TABLE 5

RESERVOIR SPECIES OF C, O, AND N AT STEADY STATE

Element	Reservoir	Percentage of Element In
C...........	CO	100.0
O...........	CO	41.5
	O_2	17.5
	O	40.9
N...........	N_2	60.3
	N	39.7

amounts of atomic oxygen at times through steady state. The same is also true for atomic nitrogen. We summarize the reservoir species of these three elements at steady state in Table 5 as determined from the new standard model. The large amounts of atomic oxygen and nitrogen are the reason for the poisoning of interstellar chemistry when many rapid neutral-neutral reactions are included in the reaction set. If the chemistry is not correctly described in these models and oxygen and nitrogen do have other reservoir species, e.g., ices in dust mantles, then the inclusion of neutral-neutral reactions in the reaction set does not have such a significant negative impact on the formation of complex species.

We conclude with the recommendation that given the large uncertainties in current gas-phase models that contain rapid neutral-neutral reactions, observers continue for the time being to utilize so-called standard models or slightly modified standard models (e.g., Herbst & Leung 1989, 1990) since these appear to be in general agreement with observed molecular abundances at early time.

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