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The sensitivity of gas-phase models of dense interstellar clouds to changes in dissociative recombination branching ratios

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Summary. The approach of Bates to the determination of neutral product branching ratios in ion-electron dissociative recombination reactions has been utilised in conjunction with quantum chemical techniques to redetermine branching ratios for a wide variety of important reactions of this class in dense interstellar clouds. The branching ratios have then been used in a pseudo time-dependent model calculation of the gas phase chemistry of a dark cloud resembling TMC-1 and the results compared with an analogous model containing previously used branching ratios. In general, the changes in branching ratios lead to stronger effects on calculated molecular abundances at steady state than at earlier times and often lead to reductions in the calculated abundances of complex molecules. However, at the so-called "early time" when complex molecule synthesis is most efficient, the abundances of complex molecules are hardly affected by the newly used branching ratios.

Key words: interstellar medium: molecules – abundances – atomic and molecular-processes

1. Introduction

One of the problems afflicting chemical models of interstellar clouds is the lack of knowledge of the rates and products of important reactions. This problem is most severe for chemical processes on the surfaces of dust grains but is also present in gas phase models, even though gas phase processes are generally better understood and have been studied in the laboratory in more detail. One of the least understood gas phase processes is dissociative recombination, a reaction in which a molecular ion recombines with an electron and dissociates into neutral fragments. Although total rate coefficients for this process as functions of temperature have been measured by a variety of techniques (see, e.g., Bardsley and Biondi, 1979; Mul and McGowan, 1980; Smith and Adams, 1984), limited measurements of what neutral fragments are produced and in what branching ratios are available only for two reactions ($H_3^+ + e$, $H_2O^+ + e$; Mitchell et al., 1983; Vallée et al., 1987). In addition, detailed quantum mechanical treatments of the process face the formidable obstacle of large numbers of possible neutral potential surfaces on which the process can occur, and have only occasionally been undertaken for polyatomic ions (Kraemer and Hazi, 1985; Michels and Hobbs, 1984). As a result, modellers have been forced to utilise results based on simplified pictures of the dissociative recombination process.

The first such picture was developed by Herbst (1977) who formulated a statistical model of the process. Shortly afterwards, Green and Herbst (1979) revised this picture somewhat and argued that upon dissociation of the neutral molecule, removal of one or more hydrogen atoms was the favoured pathway for ions containing both heavy atoms and hydrogen atoms. This viewpoint has been adopted by most modellers and would appear to be critical to gas phase syntheses of complex molecules because it preserves the heavy atom skeleton of the molecular ion which has been synthesized via a sequence of ion-molecule reactions. More recently, however, Bates (1986, 1987a) has argued that neither of these approaches contains the essence of his original (Bates, 1950) classic paper on the subject and he has reformulated a different view of the likely neutral product branching ratios.

It is the purpose of this paper to utilise the "new" approach of Bates to estimate products and branching ratios for a wide variety of molecular ion dissociative recombination reactions important in dense interstellar cloud models and to then use these results in model calculations of dense clouds. The detailed pseudo time-dependent gas phase model we have used has been discussed in the literature (Millar et al., 1987) and is a modification of the Millar and Nejad (1985) model. In Sect. 2 we discuss our approach to obtaining the desired branching ratios, whilst in Sect. 3 we discuss the results of our model calculations. Our conclusions are contained in Sect. 4.

2. Dissociative recombination

The classical theory of Bates (1950) can be summarised as follows. The process of dissociative recombination occurs in two stages: in the first stage the electrons undergo a radiationless transition which leads to the formation of a neutral molecule on a repulsive surface. In the second stage, the neutral molecule breaks apart quickly enough so that autoionization does not occur. If the molecular ion is thought of as being held together by valence bonds, the dissociative recombination process involves the enter-

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Send offprint requests to: T. J. Millar ing of the free electron into a rather localised anti-bonding orbital and the simultaneous excitation of a bound electron into the anti-bonding orbital. The resultant double excitation state leads to the rupture of the localised bond if it is repulsive in origin. Bates (1987a) has noted that even multiple bonds, such as the one in NO^+, can be broken up by this process if it is exothermic.

The major difficulty in applying this view of dissociative recombination to polyatomic molecular ions is deciding which valence bonds are preferentially disrupted. According to Bates (1986, 1987a), the bond or bonds disrupted are those involving the significant atomic positive charges on the ion. Although Bates (1986, 1987a) has in most instances deduced the charge distributions from classical valence bond considerations, we have chosen to augment this approach with modern ab initio quantum chemical calculations for those ions of well-defined structure and electronic ground state. The major result of these calculations, discussed below and incorporated into our estimates for molecules not included in our calculations, is that positive charge tends to be delocalised more than in the classical viewpoint. The number of possible neutral fragment channels is thereby increased.

Consider, as an example, the hypothetical ion $(\mathrm{H{-}A{-}B{-}H})^+$ where A and B represent heavy atoms. If the positive charge is localised on A, the possible neutral products are H + ABH and HA + BH, whereas if it is spread out evenly over A and B, the products HAB and H are also possible. In Bates' view, it is unlikely that several bonds are broken simultaneously; e.g. one does not normally see H + AB + H as a primary product although the possibility exists that primary products such as HAB can decompose secondarily. Special circumstances can arise however, in which such products appear (Bates, 1986, 1987a); typically involving one weak bond which can break simultaneously with a strong one.

The quantum chemical calculations have involved RHF/6–31 G (d) wave functions (open shell molecules were treated with restricted Hartree-Fock theory) (Hehre et al., 1986) and two approaches to the determination of atomic charges: the classical Mulliken analysis supplemented by the newer natural bond order (NBO) analysis (Reed et al., 1985; Reed and Weinhold, 1985). It is well known that calculated atomic charges are often quite dependent on basis set and method of analysis. However, if one defines a "group charge" as the overall charge on a heavy atom and its surrounding hydrogen atoms, it is found that the "group charges" vary less severely with basis set or mode of analysis. This can be seen in Table 1 where the atomic and group charges for protonated methyl amine ($CH_3NH_3^+$) are listed for both methods of analysis and a series of basis sets. Consequently, group charges have been used predominantly in deriving possible neutral products although on occasion atomic charges must be utilised. An example is the linear ion $(\mathrm{H{-}C{-}N{-}H})^+$ where calculations show the following ranges of atomic charges:

$$\begin{array}{ccccccc} +0.3 \text{ to } +0.4 & & +0.5 \text{ to } +0.6 & & -0.4 & & +0.5. \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{N} & - & \mathrm{H} \end{array}$$

Table 1. $CH_3NH_3^+$ atomic and group charges

Basis Set	N	C	H(N)	H(C)	NH_3	CH_3
	(a) Mulliken Analysis					
STO-3G	-0.39	-0.09	0.35	0.14	0.67	0.33
6-31G(d)	-0.76	-0.46	0.47	0.27	0.66	0.34
6-311G(d,p)	-0.21	-0.19	0.30	0.17	0.67	0.33
6-311++G(df,pd)	-0.25	-0.46	0.36	0.21	0.83	0.17
6-311++G(2d,2p)	+0.20	-0.09	0.19	0.10	0.77	0.23
	(b) NBO Analysis					
STO-3G	-0.29	-0.05	0.34	0.11	0.73	0.28
6-31G(d)	-0.74	-0.45	0.47	0.26	0.67	0.33
6-311G(d,p)	-0.60	-0.29	0.43	0.20	0.69	0.31
6-311++G(df,pd)	-0.61	-0.30	0.43	0.21	0.68	0.32
6-311++G(2d,2p)	-0.61	-0.30	0.43	0.21	0.68	0.32

The CH group charge is +0.9 whereas the NH group charge is only +0.1. Thus one expects the dominant product(s) of dissociative recombination to be H + CNH and, if it is exothermic, HC + NH. (This channel has been ignored here due to uncertainty over whether it is exothermic.) However, the individual atomic charges reveal a significant positive charge on the nitrogenic hydrogen, allowing the possibility of the products HCN + H. Since atomic charges are more poorly defined than group charges, we have in this and other cases somewhat arbitrarily assumed a branching ratio in the vicinity of 2 to 1 in favour of the products derived from group charges. Products derived from group charges have normally been assigned equal probabilities. However, exceptions arise for neutral products in which weak non-valence bonds exist. If sufficiently weak, these are assumed to break simultaneously with stronger bonds, in which case channels, in which the weaker bonds are maintained, are assigned branching ratios in the vicinity of 0.1.

In Table 2 we present all new dissociative recombination product channels and/or branching ratios in our model derived via the approach of Bates, who has himself (Bates 1986, 1987a) considered a subset of these reactions, although our results are not always in agreement. (Deleted channels from our previous model are not shown.) Unstable and weakly metastable species have been allowed to proceed toward their more stable forms (e.g. $CCH_2 \rightarrow C_2H_2$). Standard values for the overall rate coefficients as functions of temperature have been used in the absence of experimental studies.

In what manner do the results shown in Table 2 differ from those used in previous recent model calculations such as those of Millar and Nejad (1985), Herbst and Leung (1986a, b), and Millar et al. (1987)? In these models, the idea of Green and Herbst (1979) that limited fragmentation of the molecular ion leading to the removal of *one or two* hydrogen atoms dominates was utilised in the main. This approach is frequently in agreement with an earlier statistical treatment of Herbst (1977). For smaller ions with one heavy atom (H_3O^+, NH_4^+), the approach of Bates normally, but not always, leads to the removal of *one H atom only*. For larger ions with several heavy atoms, the approach of Bates leads to channels in which the break-up of heavy atom – heavy atom bonds occurs in addition to channels in which single hydrogen atom removal occurs. It would seem that inclusion of the former channels should reduce the abundances of complex molecules formed from ion precursors. For example, the ion $C_2H_3^+$ dissociatively recombines to form only C_2H_2 + H and C_2H + 2 H in the earlier models, whereas here we allow the possibility CH + CH_2. The breaking up of heavy atom bonds is a process which militates against the synthesis of increasingly complex species.

Table 2. New dissociative recombination rate coefficients

Reaction		Adopted Rate Coefficient ($cm^3\ s^{-1}$) $k = A\ (T/300)^{-0.50}$ A
H_3^+ + e	→ H_2 + H	1.0 (-10)
CH_2^+ + e	→ CH + H	3.0 (-7)
NH_2^+ + e	→ NH + H	3.0 (-7)
H_2O^+ + e	→ OH + H	4.0 (-7)
HCN^+ + e	→ CN + H	1.5 (-7)
	→ CH + N	1.5 (-7)
N_2H^+ + e	→ N_2 + H	0.9 (-7)[a]
	→ N + NH	0.9 (-7)[a]
CCN^+ + e	→ C_2 + N	1.0 (-7)
	→ CN + C	2.0 (-7)
NH_3^+ + e	→ NH_2 + H	1.8 (-7)
CH_3^+ + e	→ CH_2 + H	3.0 (-7)
H_3O^+ + e	→ H_2O + H	1.3 (-6)
$HCNH^+$ + e	→ HCN + H	6.0 (-8)
	→ HNC + H	1.4 (-7)
H_2CO^+ + e	→ HCO + H	3.0 (-7)
	→ CH_2 + O	3.0 (-7)
H_2NC^+ + e	→ HNC + H	1.0 (-7)
	→ NH_2 + C	1.0 (-7)
$C_2H_2^+$ + e	→ C_2H + H	1.5 (-7)
	→ CH + CH	1.5 (-7)
$C_2H_3^+$ + e	→ C_2H_2 + H	3.0 (-8)
	→ C_2H + 2H	1.35 (-7)
	→ CH + CH_2	1.35 (-7)
CH_4^+ + e	→ CH_3 + H	4.8 (-7)
	→ CH_2 + 2H	1.2 (-7)
NH_4^+ + e	→ NH_3 + H	2.0 (-7)
H_3CO^+ + e	→ H_2CO + H	3.0 (-7)
	→ CH_2 + OH	3.0 (-7)
CH_5^+ + e	→ CH_2 + H_2 + H	4.8 (-7)
	→ CH_3 + H_2	6.0 (-8)
	→ CH_4 + H	6.0 (-8)
$C_2H_4^+$ + e	→ C_2H_3 + H	1.5 (-7)
	→ CH_2 + CH_2	1.5 (-7)
C_3H^+ + e	→ C_3 + H	1.0 (-7)
	→ C_2 + CH	1.0 (-7)
	→ C + C_2H	1.0 (-7)
$C_3H_2^+$ + e	→ C_3H + H	1.5 (-7)
	→ C_2H + CH	1.5 (-7)
$C_3H_3^+$ + e	→ C_3H_2 + H	1.5 (-7)[b]
	→ C_2H_2 + CH	1.5 (-7)[b]
$C_3H_4^+$ + e	→ C_3H_3 + H	1.5 (-7)
	→ CH_2 + C_2H_2	1.5 (-7)
$C_3H_5^+$ + e	→ C_3H_4 + H	1.5 (-7)
	→ C_2H_3 + CH_2	1.5 (-7)
C_4^+ + e	→ C_3 + C	1.5 (-7)
	→ C_2 + C_2	1.5 (-7)
C_4H^+ + e	→ C_4 + H	7.5 (-8)
	→ C_3 + CH	7.5 (-8)
	→ C_2 + C_2H	7.5 (-8)
	→ C + C_3H	7.5 (-8)
$C_4H_2^+$ + e	→ C_4H + H	1.0 (-7)
	→ C_3H + CH	1.0 (-7)
	→ C_2H + C_2H	1.0 (-7)
$C_4H_3^+$ + e	→ C_4H_2 + H	1.0 (-7)
	→ C_3H_2 + CH	1.0 (-7)
	→ C_2H + C_2H_2	1.0 (-7)
C_5^+ + e	→ C_4 + C	1.5 (-7)
	→ C_3 + C_2	1.5 (-7)
C_5H^+ + e	→ C_5 + H	6.0 (-8)
	→ C_4 + CH	6.0 (-8)
	→ C_3 + C_2H	6.0 (-8)
	→ C_2 + C_3H	6.0 (-8)
	→ C + C_4H	6.0 (-8)
$C_5H_3^+$ + e	→ C_5H_2 + H	1.0 (-7)
	→ C_4H_2 + CH	1.0 (-7)
	→ C_3H_2 + C_2H	1.0 (-7)
	→ C_5H + H + H	1.0 (-8)[c]
$C_5H_5^+$ + e	→ C_5H_4 + H	1.5 (-7)
	→ C_4H_2 + CH_3	1.5 (-7)
$C_6H_3^+$ + e	→ C_6H + H + H	1.0 (-7)[c]
	→ C_5H_2 + CH	1.0 (-7)
	→ C_4H_2 + C_2H	1.0 (-7)
C_7^+ + e	→ C_4 + C_3	1.5 (-7)
	→ C_5 + C_2	1.5 (-7)
CH_3CO^+ + e	→ CH_2CO + H	1.0 (-7)
	→ C_2H_2 + OH	1.0 (-7)
	→ CH_3 + CO	1.0 (-7)
HC_3O^+ + e	→ C_3O + H	1.5 (-7)
	→ C_2H + CO	1.5 (-7)
$C_3H_2O^+$ + e	→ C_2H_2 + CO	1.5 (-7)
	→ C_3O + 2H	1.5 (-7)
$CH_3OH_2^+$ + e	→ CH_3OH + H	1.5 (-7)
	→ CH_3 + H_2O	1.5 (-7)
	→ CH_2 + H + H_2O	3.0 (-8)
HC_3N^+ + e	→ C_3N + H	1.5 (-7)
	→ C_2H + CN	1.5 (-7)
$H_2C_3N^+$ + e	→ HC_3N + H	1.0 (-7)
	→ C_2H + HNC	1.0 (-7)
	→ C_3H + NH	1.0 (-7)
$H_4C_3N^+$ + e	→ H_3C_3N + H	1.0 (-7)
	→ C_2H_4 + CN	1.0 (-7)
	→ C_2H_3 + HNC	1.0 (-7)
$H_2C_5N^+$ + e	→ HC_5N + H	1.0 (-7)
	→ C_5N + 2H	1.0 (-8)[c]
	→ C_4H + HNC	1.0 (-7)
	→ C_2H_2 + C_3N	1.0 (-7)
$H_4C_2N^+$ + e	→ CH_3CN + H	1.0 (-7)
	→ CH_3 + HNC	2.0 (-7)
$H_4C_4N^+$ + e	→ CH_3C_3N + H	1.5 (-7)
	→ C_3H_3 + HNC	1.5 (-7)

NOTE: a(-b) denotes a x 10^{-b}.

[a] Temperature coefficient $(T/300)^{-0.99}$

[b] Results from both linear and cyclic forms

[c] Included to close model despite predictions of Bates' theory.

3. Model calculations and discussion

The gas phase model utilised for these calculations is an updated version of "Model 5" of Millar, Leung, and Herbst (1987) and contains 131 species and 612 reactions. It is pseudo time-dependent in the sense that molecular abundances evolve under fixed physical conditions. "Model 5" itself is a variation of the Millar and Nejad (1985) model with a small number of additional reactions and product channels which enable this smaller model to reproduce the results of the larger Herbst and Leung (1986a) model. The model is designed for dark clouds such as TMC-1; the

Table 3. Additional H_3O^+ proton transfer reactions

Reaction	Rate Coefficient(cm^3 s^{-1})
$H_3O^+ + HCN \longrightarrow HCNH^+ + H_2O$	4.0(-9)[a]
$H_3O^+ + HNC \longrightarrow HCNH^+ + H_2O$	4.0(-9)
$H_3O^+ + NH_3 \longrightarrow NH_4^+ + H_2O$	2.2(-9)[a]
$H_3O^+ + H_2CO \longrightarrow H_3CO^+ + H_2O$	3.4(-9)[a]
$H_3O^+ + C_2H_3 \longrightarrow C_2H_4^+ + H_2O$	2.0(-9)
$H_3O^+ + C_3 \longrightarrow C_3H^+ + H_2O$	2.0(-9)
$H_3O^+ + C_3H \longrightarrow C_3H_2^+ + H_2O$	2.0(-9)
$H_3O^+ + C_3H_2 \longrightarrow C_3H_3^+ + H_2O$	3.0(-9)
$H_3O^+ + C_3H_3 \longrightarrow C_3H_4^+ + H_2O$	2.0(-9)
$H_3O^+ + C_3H_4 \longrightarrow C_3H_5^+ + H_2O$	2.0(-9)
$H_3O^+ + C_4 \longrightarrow C_4H^+ + H_2O$	1.1(-9)
$H_3O^+ + C_4H \longrightarrow C_4H_2^+ + H_2O$	1.1(-9)
$H_3O^+ + C_4H_2 \longrightarrow C_4H_3^+ + H_2O$	1.1(-9)[b]
$H_3O^+ + C_3N \longrightarrow HC_3N^+ + H_2O$	2.0(-9)
$H_3O^+ + CH_2CO \longrightarrow CH_3CO^+ + H_2O$	2.0(-9)[a]
$H_3O^+ + CH_3OH \longrightarrow CH_3OH_2^+ + H_2O$	2.5(-9)[a]
$H_3O^+ + CH_3CN \longrightarrow CH_3CNH^+ + H_2O$	4.7(-9)[a]

[a] measured at 300 K (Anicich and Huntress 1986)

[b] Dheandhanoo et al. (1986)

cloud temperature is 10 K, the H_2 density 1.0 10^4 cm^{-3}, the visual extinction (edge to centre) is 10 mag, and low metal abundances are used. Our current model differs from "Model 5" in several salient ways in addition to the utilisation of new dissociative recombination branching ratios: the latest value of the $CH_3^+ + H_2$ radiative association reaction (Bates, 1987b) has been included as have some additional reactions involving H_3O^+ (see Table 3). As will be discussed below, this species is much more abundant than in previous models and its chemistry must be considered more carefully. The rate coefficients utilised for ion-polar neutral reactions are not the rapid ones advocated by Adams et al. (1985), for which some low temperature experimental evidence is available (Marquette et al., 1987), since the model calculation of Herbst and Leung (1986b) shows the effect of large ion-polar rate coefficients to be ordinarily rather small.

The results of our calculations are shown in Table 4 for two times – steady state, which is achieved after 10^7–10^8 yr, and the so-called "early time" (3.16 10^5 yr), at which complex molecules achieve a maximum abundance. Three calculations have been undertaken: the results labelled "Old" are those in which the previous dissociative recombination branching ratios (Leung et al., 1984; Millar et al., 1987) have been used. Calculations in which the new branching ratios have been included are designated by $f = 0.0$ and $f = 0.1$. The $f = 0.0$ model designates one in which the reaction between H_3O^+ and electrons produces $H_2O + H$ only, as suggested by Bates (1986, 1987a), instead of producing both $H_2O + H$ and $OH + H_2$ (2 H). This change leads to a dramatic effect in which the OH abundance at all times drops significantly and H_2O replaces O_2 as the dominant molecular repository of oxygen. Since it is far from clear that even in Bates' model "no" OH is formed, we have also performed model calculations with a branching ratio of 0.1 for the $OH + H_2$ (2 H) channel ("$f = 0.1$"). Steady-state model results as a function of f have been published by Sternberg et al., 1987) who, however, do not apply Bates' approach to the large number of ions considered here.

The results of our model calculations are best discussed by dividing the many molecules in the model into groups.

3.1. OH, H_2O, O_2, NO, N_2

As mentioned above, the use of $f = 0.0$ reduces OH considerably at all times and enhances H_2O into the dominant oxygen-containing species. Species produced from OH are also reduced significantly: examples are O_2 (produced via OH + O), NO (produced via OH + N) and N_2 (produced via NO + N). The abundances of atomic O, N, and C also rise considerably at steady state (especially N and C) since at this time these species are depleted primarily by neutrals produced from OH. Changing $f = 0.0$ to $f = 0.1$ reduces all of these effects considerably; at steady-state O_2 has an abundance greater than H_2O whereas OH has only decreased a factor of 2.6 from its previously calculated abundance. The reason that OH decreases by only a factor of 2.6 as f decreases from 0.5 (old calculations) to 0.1 is that H_3O^+ increases in abundance.

The calculated OH abundances with $f = 0.0$ are $\approx 10^{-9}$ at both early time and steady-state. These values are significantly below the observed value of 3 10^{-7} in TMC–1 (Irvine et al., 1985). Sternberg et al. (1987) are able to enhance the calculated OH abundance at steady state to 3.3 10^{-8} via photodissociation of H_2O through internally generated UV photons. Such photodissociation processes are not considered in this model. Our $f = 0.1$ model is also in good agreement with observation.

3.2. NH_3, HCN, HNC

The fractional abundance of ammonia increases at steady-state in the new calculation for several reasons. First, in analogy with H_2O, its precursor ion NH_4^+ can only dissociatively recombine into $NH_3 + H$ so that protonation of NH_3 via the abundant ions H_3^+, HCO^+, H_3O^+ is no longer a depletion mechanism. Secondly, the abundance of N_2, an ammonia precursor, is high for $f = 0.1$, especially at steady-state. Less importantly, the increase in atomic N at steady-state, via cosmic ray ionisation followed by hydrogenation, also enhances the formation rate of NH_3. The increase in NH_3 leads to an increase in molecules derived from ammonia such as HCN and HNC. This increase is especially strong at steady-state.

The newly calculated ammonia abundances at steady-state are in the range 4 10^{-6} – 4 10^{-7} and are more than adequate to explain the observational results (2 10^{-8} in TMC–1; Irvine et al., 1985) despite the exclusion of the $N + H_3^+$ mechanism for NH_3 production from our models (Herbst et al., 1987). At early time the calculated values are somewhat lower, but still in reasonable agreement with observation. The newly calculated HNC and HCN abundances are somewhat higher than the observed value of 2 10^{-8} (Irvine et al., 1985) in TMC–1.

3.3. Molecular ions

Although the fractional ionic abundance is not significantly altered via the new dissociative recombination branching ratios, the abundances of the dominant molecular ions are affected. In particular H_3O^+ becomes the major molecular ion in the $f = 0.0$ model, especially at steady state where its fractional abundance of 4.3×10^{-9} is double that of H_3^+ and HCO^+ combined. The effect is smaller in the $f = 0.1$ calculation. The observed fractional

Table 4. Detailed comparison of fractional abundances calculated with and without new recombination branching ratios

	Fractional Abundances With Respect to H_2					
	Early Time (3.16×10^5 yr)			Steady State (1.0×10^8 yr)		
Species	OLD	f = 0.0	f = 0.1	OLD	f = 0.0	f = 0.1
C	2.4(-5)	4.8(-5)	4.1(-5)	3.2(-10)	6.3(-8)	1.2(-8)
O	2.3(-4)	2.3(-4)	2.2(-4)	3.5(-5)	9.7(-5)	4.6(-5)
N	3.9(-5)	4.2(-5)	4.1(-5)	9.8(-7)	4.2(-5)	9.6(-6)
C_2	3.8(-9)	2.6(-9)	2.4(-9)	1.0(-10)	3.8(-11)	1.0(-9)
O_2	1.6(-6)	4.1(-8)	2.8(-7)	8.3(-5)	3.9(-7)	6.4(-5)
N_2	1.7(-6)	7.6(-8)	4.3(-7)	2.1(-5)	2.7(-7)	1.4(-5)
CH	2.2(-9)	3.2(-9)	3.4(-9)	1.5(-10)	1.8(-11)	3.9(-11)
NH	7.7(-11)	4.3(-11)	9.2(-11)	4.1(-9)	8.9(-11)	1.1(-8)
OH	1.6(-7)	7.3(-9)	4.3(-8)	6.8(-7)	7.2(-10)	2.6(-7)
CO	9.3(-5)	7.6(-5)	8.5(-5)	1.5(-4)	1.5(-4)	1.4(-4)
CN	3.7(-8)	1.0(-8)	2.0(-8)	8.1(-10)	4.3(-10)	9.4(-9)
NO	2.5(-8)	8.4(-10)	5.4(-9)	1.7(-7)	1.9(-10)	6.9(-8)
CH_2	6.1(-8)	1.9(-7)	1.9(-7)	5.6(-10)	1.2(-9)	2.8(-9)
NH_2	4.8(-11)	1.2(-11)	1.3(-11)	2.6(-9)	4.0(-11)	1.3(-9)
H_2O	1.3(-5)	4.3(-5)	3.5(-5)	3.8(-6)	1.1(-4)	3.3(-5)
HCN	4.3(-8)	1.2(-7)	1.2(-7)	7.9(-10)	3.3(-8)	2.8(-7)
HNC	2.6(-8)	1.7(-7)	1.7(-7)	2.2(-9)	8.0(-8)	6.8(-7)
HCO	2.9(-9)	1.2(-9)	1.2(-9)	5.8(-11)	8.2(-12)	1.4(-11)
CCH	2.3(-8)	2.5(-8)	2.6(-8)	1.7(-9)	1.6(-10)	2.7(-10)
CO_2	8.0(-7)	5.7(-7)	5.6(-7)	1.0(-8)	1.1(-8)	6.5(-9)
NH_3	7.9(-9)	2.1(-8)	2.7(-8)	5.6(-8)	4.2(-7)	3.8(-6)
H_2CO	4.7(-6)	1.1(-6)	1.1(-6)	1.6(-8)	4.7(-9)	3.3(-9)
CH_3	1.0(-8)	2.5(-9)	2.4(-9)	4.6(-10)	2.1(-11)	4.1(-11)
CH_4	1.9(-5)	1.5(-5)	1.4(-5)	1.1(-7)	1.5(-7)	7.4(-8)
C_2H_2	7.4(-7)	7.7(-7)	7.4(-7)	8.2(-9)	1.8(-8)	2.9(-9)
C_2H_3	2.4(-7)	1.9(-7)	1.9(-7)	1.2(-8)	1.6(-9)	2.7(-9)
C_3	2.6(-9)	1.7(-9)	1.5(-9)	6.5(-11)	2.4(-13)	2.9(-13)
C_3H	3.9(-7)	3.7(-7)	3.6(-7)	3.0(-9)	1.5(-10)	1.1(-10)
C_3H_2	1.6(-7)	1.5(-7)	1.5(-7)	9.9(-10)	4.0(-10)	1.4(-10)
C_3H_3	7.1(-9)	4.8(-10)	4.7(-10)	3.2(-12)	8.3(-14)	6.2(-14)
C_3H_4	7.1(-9)	2.8(-9)	3.0(-9)	3.4(-12)	1.3(-12)	6.0(-13)
C_4	1.8(-9)	8.4(-10)	7.7(-10)	9.3(-12)	1.0(-13)	1.3(-13)
C_4H	2.0(-7)	1.0(-7)	9.5(-8)	1.2(-12)	6.7(-13)	4.0(-14)
C_4H_2	1.2(-8)	5.1(-9)	4.9(-9)	4.5(-13)	2.6(-13)	2.8(-14)
HC_3N	7.2(-9)	4.7(-9)	4.6(-9)	1.8(-12)	1.5(-11)	3.0(-12)
C_3N	4.8(-10)	7.1(-11)	6.9(-11)	7.6(-13)	7.4(-14)	2.6(-14)
CH_2CO	6.5(-8)	3.3(-8)	3.3(-8)	1.7(-10)	1.4(-10)	6.7(-11)
CH_3OH	7.0(-8)	1.6(-7)	1.3(-7)	7.7(-11)	1.7(-9)	4.6(-10)
CH_3CN	2.2(-8)	1.2(-8)	1.2(-8)	2.7(-11)	7.4(-12)	1.1(-10)
e	4.8(-8)	4.6(-8)	4.6(-8)	5.2(-8)	4.2(-8)	4.8(-8)
H^+	5.4(-10)	2.8(-10)	3.2(-10)	6.4(-10)	1.0(-10)	2.5(-10)
He^+	5.4(-10)	5.9(-10)	5.7(-10)	3.7(-10)	4.2(-10)	3.8(-10)
C^+	9.1(-10)	5.2(-10)	6.5(-10)	9.0(-10)	3.6(-10)	5.5(-10)
H_3^+	2.2(-9)	1.7(-9)	1.8(-9)	3.6(-9)	1.2(-9)	2.3(-9)
HCO^+	2.1(-9)	1.1(-9)	1.3(-9)	5.5(-9)	8.4(-10)	2.4(-9)
N_2H^+	2.0(-11)	7.5(-13)	4.3(-12)	3.1(-10)	1.7(-12)	1.5(-10)
H_3O^+	2.3(-9)	3.2(-9)	3.1(-9)	9.6(-10)	4.3(-9)	2.5(-9)
CH_3^+	7.0(-11)	8.6(-11)	8.0(-11)	3.1(-13)	1.8(-13)	1.9(-13)
CH_5^+	9.4(-10)	8.6(-10)	8.3(-10)	6.2(-12)	2.5(-12)	2.9(-12)

Note: a(-b) denotes a x 10^{-b}.

abundance for HCO^+ in TMC–1 of 8 10^{-9} (Irvine et al., 1985) exceeds all of our calculated values by up to an order of magnitude. The N_2H^+ ion has a dramatically reduced abundance of $\sim 10^{-12}$ at both times considered for the $f = 0.0$ model; this value is far too low to agree with the observed value of $\sim 10^{-9}$ in TMC–1 and L 134 N (Irvine et al., 1985). The calculation with $f = 0.1$ is somewhat better, but even our old model is low except at steady state.

3.4. *Hydrocarbons*

The principal concern of this paper is how the new dissociative recombination branching ratios affect the synthesis of complex molecules such as hydrocarbons. Use of these branching ratios results in more extensive break up of molecular ions than in previous models; naively one expects smaller abundances of complex neutrals since the synthetic power of ion-molecule chemistry is reduced. In general, this effect is observed *but is only significant at steady state*. Even then, the diminution of calculated fractional abundances varies greatly from one molecule to another and depends on specific reaction networks and specific branching ratios. More importantly, at early time, when gas phase syntheses of complex molecules are at their peak efficiency, use of the new dissociative recombination branching ratios ordinarily results in only slightly different abundances. The reason is that complex molecule syntheses is sufficient to withstand a small drop in efficiency. Thus, a major conclusion of this paper is that at early time, complex molecules are still synthesised efficiently. The increasing sensitivity of complex molecule abundances to dissociative recombination branching ratios as time increases is shown in Fig. 1 for C_3H.

It is interesting to point out that the new synthetic paths to complex molecules can be different and more complex than was heretofore the case. Consider the acetylene molecule C_2H_2. Previously formed primarily via dissociative recombination of $C_2H_3^+$ and $C_2H_4^+$, it is now produced at least partially via the sequence:

$$\begin{aligned}
C_2H_3^+ + e &\rightarrow C_2H + H + H\\
C^+ + C_2H &\rightarrow C_3^+ + H\\
C_3^+ + H_2 &\rightarrow C_3H^+ + H\\
C_3H^+ + H_2 &\rightarrow C_3H_3^+ + h\nu\\
C_3H_3^+ + O &\rightarrow C_2H_2 + HCO^+.
\end{aligned}$$

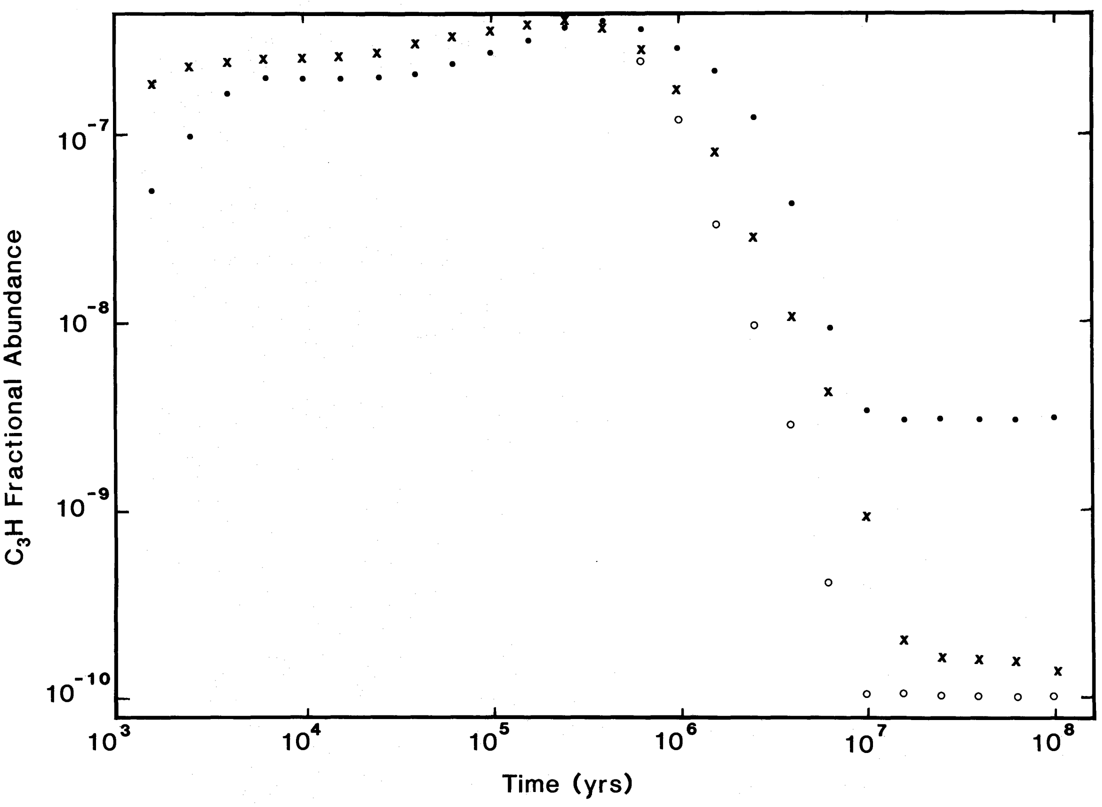

Fig. 1. The fractional abundance of C_3H relative to H_2 is shown as a function of time for the calculations listed in Table 1. Old model (···); $f = 0.0$ model (× × ×); $f = 0.1$ (○○○)

As noted in a variety of recent models (Millar and Nejad, 1985; Leung et al., 1984; Herbst and Leung, 1986a, b) calculated early-time abundances of complex species are normally somewhat large compared with observation. This still remains the case. For example our calculated abundances for C_3H, C_3H_2, and C_4H at early time are $\approx 4\ 10^{-7}$, $2\ 10^{-7}$, and $1\ 10^{-7}$ respectively (note the lack of differences among all three calculations) as compared with observed values in TMC–1 of $5\ 10^{-10}$, $1.5\ 10^{-8}$, and $2\ 10^{-8}$ respectively (Thaddeus et al., 1985; Madden et al., 1986; Irvine et al., 1985). It is now even more the case that calculated abundances of complex hydrocarbons at steady-state are too low, unless a variety of O-atom reactions do not proceed (Millar et al., 1987). For example, our calculated steady-state abundances of C_3H, C_3H_2, and C_4H are ($f = 0.0$) $1.5\ 10^{-10}$, $4.0\ 10^{-10}$, and $6.7\ 10^{-13}$ respectively. The low observed abundance of C_3H may be due to a neutral-neutral depletion reaction with atomic oxygen, which is not included in our model. It is interesting to note that the observed fractional abundance of C_5H in TMC–1 is also low $- 3.5\ 10^{-10}$ (Cernicharo et al., 1987).

3.5. Other complex molecules

In addition to hydrocarbons, our model contains species such as CH_3OH, CH_3CN, HC_3N, and C_3N. Methanol is produced from the precursor ion $CH_3OH_2^+$, which in turn derives from the radiative association reaction between CH_3^+ and H_2O. Since H_2O is more abundant in our new ($f = 0.0$ and 0.1) calculations, one expects an increase in the methanol abundance. This increase is present, as can be seen in Table 4. However, our use of a new and more rapid rate coefficient for the radiative association reaction between CH_3^+ and H_2 (Bates, 1987b) reduces the CH_3^+ abundance so that calculated values of the methanol abundance do not really exceed older values (e.g. Herbst and Leung, 1986a).

Methyl cyanide (CH_3CN) shows an interesting effect: the new dissociative recombination branching ratios do not change its abundance significantly at early time but at steady state the $f = 0.0$ calculation shows a decrease (factor of 4) whereas the $f = 0.1$ calculation shows an increase (factor of 4). Why is CH_3CN synthesised so much more efficiently when $f = 0.1$? The major cause is the increased abundance of HCN, which reacts with CH_3^+ via radiative association to produce the ionic precursor to CH_3CN. The increased HCN is due in turn to the increased NH_3 abundance since HCN is formed via a sequence of reactions commencing with $C^+ + NH_3$. Ammonia is especially abundant for $f = 0.1$ because of the high abundance of N_2, its precursor species. The observed CH_3CN fractional abundance in TMC–1 of $\sim 10^{-9}$ (Irvine et al., 1985) is in between the early time and steady-state results.

Finally, HC_3N is not greatly affected at early time but increases dramatically at steady state for $f = 0.0$ due to a large increase in the atomic nitrogen abundance, which reacts with hydrocarbon ions to produce ionic precursors to HC_3N. Still, good agreement with observations in TMC–1 is only achieved at early time. The C_3N radial is significantly diminished at all times for both $f = 0.0$ and $f = 0.1$ because it is no longer produced via the dissociative recombination between $H_2C_3N^+$ and electrons, but instead derives mainly from the neutral-neutral reaction between N and C_3H. If this reaction does not proceed, C_3N is produced via $C_4N^+ +$ electrons at a still lower rate. The calculated C_3N abundances at early time with the new dissociative recombination branching ratios are more than one order of magnitude below the observed value in TMC–1 (Irvine et al., 1985) whereas the old calculated value is in better agreement with observation.

4. Conclusions

Using dissociative recombination branching ratios derived from the theory of Bates (1986, 1987a) with the aid of quantum chemical techniques, we have investigated their effect on a pseudo time-dependent model of dark interstellar clouds such as TMC–1. In general, we have found that differences between newly calculated molecular abundances and those calculated with the older branching ratios are more severe at steady state, reached after 10^7–10^8 yr, than at earlier times. There are exceptions to this assertion, however. The abundances of many complex species (especially hydrocarbons) are reduced, reflecting the addition of dissociative recombination channels in which large molecular ions break up rather than just losing a hydrogen atom or atoms. Still, the effect at "early times" (3.16 10^5 yr), at which time complex molecules are most effectively synthesised, is normally so small for complex molecules as to be unimportant. One rather large exception is the C_3N radial which is calculated to have a severely reduced abundance.

The abundances of smaller molecules do not show as systematic an effect as the more complex hydrocarbons. Some increase whilst others decrease. One uniquely important dissociative recombination reaction is that between H_3O^+ and electrons. In Bates' approach, only $H_2O + H$ is produced whereas in older treatments OH is another major product. The use of Bates' approach leads to H_2O becoming the major molecular repository of the oxygen abundance instead of O_2 and results in far too little OH to explain its observed abundance. The OH can be recovered via photodissociation of H_2O (Sternberg et al., 1987) or via the assumption that some OH is produced in $H_3O^+ + e$. We have performed model calculations in which OH is produced with a branching ratio f of 0.1. In general, the results of this model are closer to the older values than the $f = 0.0$ model, although there are exceptions to this statement. In particular, species such as NH_3, HCN, HNC, and CH_3CN are strongly enhanced at steady state when $f = 0.1$.

The use of the branching ratios for dissociative recombination reactions as advocated by Bates (1986, 1987a) does not appear to have generally worsened or improved the agreement between theory and observation, although a few specific cases (N_2H^+, C_3N, OH) of worse agreement exist. *It is important that laboratory measurements and/or detailed theoretical approaches be undertaken shortly to determine the proper branching ratios to use.* Indeed, experimental measurements and detailed theory are still urgently needed for a wide range of other reactive processes utilised in gas phase models of dense interstellar clouds, particularly neutral-neutral reactions at low temperature (Millar et al., 1987). Without definitive information on dissociative recombination and other processes, models of interstellar clouds contain an additional aura of uncertainty.

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