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ASSOCIATION REACTIONS OF Fe^+ WITH HYDROCARBONS: IMPLICATIONS FOR DENSE INTERSTELLAR CLOUD CHEMISTRY

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ABSTRACT

Reactions of Fe^+ with several small hydrocarbons have been studied using the selected-ion flow tube (SIFT) technique at 0.35 torr and 294 K. These reactions, which occur solely by association, are expected to have a considerable influence upon the ratio of neutral to ionized Fe-bearing species within dense interstellar clouds. Furthermore, since Fe^+ has generally been considered as one of the principal charge-carrying species within dense clouds, the reactions discussed here also have a very significant bearing on the overall degree of ionization within interstellar clouds. We discuss prospects for the formation of Fe-containing neutrals such as FeCO, FeC_2H_n, and FeC_4H_n ($n = 1, 2$) in dissociative recombination reactions of the adduct ions expected from the reaction of Fe^+ with the abundant interstellar hydrocarbons C_2H_2 and C_4H_2.

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

1. INTRODUCTION

Iron is one of the most abundant elements in the universe. Within dense interstellar clouds, iron is expected to be markedly depleted in the gas phase, with most Fe being "locked up" as a component of dust grains in such clouds (Duley & Millar 1978; Jones 1990). The extent to which gas-phase iron is depleted within dense interstellar clouds is as yet unknown: atomic Fe is not detectable within dense clouds, and searches for the Fe-containing molecules FeO (Merer, Walmsley, & Churchwell 1982) and FeCO (Kasai et al. 1995) within dense clouds have proven negative. A comparison of upper limits to the abundances of several molecules containing the cosmically abundant refractory elements Si, P, Mg, Na, Al, Fe, Ti, and Ca (Turner 1991) indicates that gas-phase iron is depleted by a factor of ~ 100 within cold diffuse clouds. This is more severe than the extent to which Si is depleted in the gas phase in similar objects, and if the trend in gas-phase depletion of Fe is similar to that seen for Si (as evidenced by the absence within dense clouds of SiO, which is expected to be the dominant form of gas-phase Si within such objects; Herbst et al. 1989), a depletion factor of 10^6 or higher may apply for Fe within cold, dense interstellar clouds. If Fe is so heavily depleted, then a total dense-cloud abundance of $\sim 10^{-11}$ $n(H_2)$, or less, would apply for all gas-phase iron.

The scenario presented above contrasts somewhat with the abundances used in the modeling of gas-phase dense-cloud chemistry: such models have traditionally employed less drastic depletion of refractory elements. For example, Herbst & Leung (1986) have calculated values of $n(Fe) = 1.4 \times 10^{-9} n(H_2)$ and $n(Fe^+) = 4.6 \times 10^{-9} n(H_2)$ at early times within a "model" interstellar cloud, while Millar et al. (1991) have derived similar early-time values: $n(Fe) = 5.3 \times 10^{-10} n(H_2)$ and $n(Fe^+) = 5.5 \times 10^{-9} n(H_2)$. Fe^+ is therefore a major ion within these models, its abundance exceeded only by Mg^+ and by HCO^+ in Herbst & Leung's (1986) model, while Fe^+ is the most abundant ion according to the reaction network employed by Millar et al. (1991). These models estimate that Fe^+ accounts for approximately 15% of the total positive ion abundance within dense clouds.

The high Fe^+/Fe ratio in these models of interstellar cloud chemistry results from the relative inefficiency of loss processes for Fe^+ when compared to pathways for its production. For example, in the chemical model constructed using the UMIST ratefile (Millar et al. 1991), the important interstellar ions H^+, H_3^+, C^+, CH^+, CH_3^+, Si^+, and HCO^+ are all involved in rapid charge-transfer (or dissociative charge-transfer) reactions

$$X^+ + Fe \rightarrow Fe^+ + X , \qquad (1)$$

which produce Fe^+, while the sole loss processes considered for Fe^+ (excluding the mutual neutralization reactions of Fe^+ with the presumed dense cloud constituents H^-, C^-, and S^-) are the charge-transfer process

$$Fe^+ + Na \rightarrow Fe + Na^+ , \qquad (2)$$

and the radiative recombination reaction

$$Fe^+ + e \rightarrow Fe + h\nu . \qquad (3)$$

Both these Fe^+ loss processes are assumed to be inefficient under interstellar cloud conditions: $k_2 = 1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, and $\alpha_3 = 3.4 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at $T = 10$ K (Millar et al. 1991).

Given the high abundance of Fe^+ according to model calculations, the reactions of Fe^+ with cloud molecules are potentially of much interest: among other concerns, determination of the depletion of iron and other refractory elements within dense clouds relies on a detailed knowledge of their gas-phase reaction chemistry under interstellar conditions. This point has been emphasized by Millar (1982), who has noted that metal ion radiative association reactions (including those of Fe^+) and subsequent "switching" reactions are potentially of much importance in influencing the

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chemical evolution of, and degree of ionization within, dense interstellar clouds. Despite their possible importance, few reactions of Fe^+ with interstellar molecules have been studied previously. For example, the ion/molecule reaction compilation of Anicich (1993) features the reactions of Fe^+ with only 11 different neutrals: these neutrals are either unreactive with Fe^+ (e.g., H_2, CH_4) or are of negligible abundance within dense interstellar clouds (e.g., C_3H_8, O_3), so the impression that Fe^+ is an unreactive dense-cloud constituent is understood easily. Recently, studies of Fe^+ reactions with polycyclic aromatic hydrocarbons (PAHs) have been reported (Dunbar, Uechi, & Asamoto 1994; Boissel 1994), suggesting that a significant product channel in such reactions is the formation of $Fe(PAH^+)$ adducts via radiative association. However, the reaction chemistry of Fe^+ that has been investigated experimentally to date has omitted the question of this ion's reactivity with several classes of small molecules that are important constituents of interstellar clouds. We have recently embarked upon a series of studies designed to redress this situation (Baranov & Bohme 1995; Baranov, Javahery, & Bohme 1995; Baranov et al. 1996). In the present work, we outline recent results of selected-ion flow tube (SIFT) studies of the reactions of Fe^+ with unsaturated hydrocarbons (Becker 1995). We suggest also that reactions of this type have a considerable effect upon the distribution of gas-phase Fe-containing species within clouds, and—reiterating Millar's (1982) suggestion—they are likely to have a significant effect also upon the overall degree of ionization within dense clouds.

2. DISCUSSION

The reactions discussed here were obtained using a selected-ion flow tube (SIFT), which has been described previously (Mackay et al. 1980; Raksit & Bohme 1983). All measurements were performed at a helium buffer gas pressure of 0.35 ± 0.01 torr and at a temperature of 294 ± 3 K. Methods of ion generation employed, as well as further details of the reaction chemistry, are discussed elsewhere (Becker 1995).

2.1. *Assumptions Concerning Efficiency of Radiative Association Reactions of* Fe^+ *with Hydrocarbons*

Throughout this work, we have assumed that the observed effective bimolecular rate coefficient for the (presumably) termolecular association reactions of Fe^+ with C_mH_n, studied under our laboratory conditions of 294 K and 0.35 torr of helium, is equal to the rate coefficient for the corresonding radiative association reaction at a cloud temperature of 10 K. This is obviously a rather gross assumption and may well not hold with any real degree of accuracy: however, it is generally accepted that reactions that proceed efficiently by termolecular association (under "high-pressure" laboratory conditions such as those that pertain within the SIFT) will also proceed by radiative association with reasonable efficiency at cold cloud temperatures.

Few examples exist of radiative association reactions that have been studied at temperatures and pressures appropriate to interstellar cloud chemistry. A larger number of association reactions have been studied at low temperature but at a pressure regime likely to favor termolecular association as the dominant means of stabilization, or at sufficiently low pressures to avoid competition from termolecular processes but at room temperature. Both the latter cases require extrapolation to low temperature or to low pressure in order to model the circumstance of radiative association under interstellar cloud conditions, and several models (see, for example, Bates & Herbst 1988; Smith, McEwan, & Gilbert 1989) have been developed with these goals in mind. The extrapolation of low-temperature, low-pressure radiative association rates from measurements at comparatively high temperatures and pressures, such as we attempt here, is fraught with considerable uncertainty. Nevertheless, some justification for the assumptions we have made in the present work may be obtained by a comparison of the termolecular and radiative association rate coefficients for the reactions of CH_3^+ with important interstellar neutrals:

1. The termolecular association reactions of CH_3^+ with HCN and with CH_3CN are rapid under SIFT conditions, with effective bimolecular rate coefficients (at 0.30 torr and 300 ± 5 K) of 2.0×10^{-9} cm^3 molecule^{-1} s^{-1} and 4.0×10^{-9} cm^3 molecule^{-1} s^{-1}, respectively (Schiff & Bohme 1979; Knight, Freeman, & McEwan 1986). The corresponding radiative association processes have also been observed under low-pressure conditions (McEwan et al. 1980, 1989) and are expected to be rapid at low temperatures: the UMIST ratefile uses a rate coefficient of 9.0×10^{-9} cm^3 molecule^{-1} s^{-1} for $CH_3^+ + HCN$ (Millar et al. 1991), while Herbst & McEwan (1990) have estimated a radiative association rate coefficient of 8.4×10^{-9} cm^3 molecule^{-1} s^{-1} for the reaction of $CH_3^+ + CH_3CN$. This level of agreement is perhaps not surprising for reactions that, at high pressure or at low temperature, occur as more-or-less "saturated" processes (i.e., most collisions lead to adduct formation).
2. Another association reaction to have received study as both a termolecular and a radiative process is that of $CH_3^+ + H_2$. An ion-trap study at 13 K has yielded a rate coefficient of 1.8×10^{-13} cm^3 molecule^{-1} s^{-1} for the radiative association of $CH_3^+ + H_2$ (Barlow, Dunn, & Schauer 1984), while a SIFT study at 295 K has determined a termolecular rate coefficient of 1.1×10^{-28} cm^6 molecule^{-2} s^{-1} (Smith, Adams, & Alge 1982), which corresponds to an effective bimolecular rate coefficient of 1.2×10^{-12} cm^3 molecule^{-1} s^{-1} at 0.35 torr of helium. The reaction of $CH_3^+ + H_2$ provides a more convincing example of order-of-magnitude agreement between SIFT termolecular and low-temperature radiative association rate coefficients, since the process is far from "saturation" under room-temperature SIFT or low-temperature ion-trap conditions.

The association reactions of Fe^+ with the unsaturated hydrocarbons C_2H_2, C_2H_4, CH_3CCH, and C_4H_2, as detailed within the present study, are all of comparatively high efficiency under our SIFT laboratory conditions: hence, we feel justified in the assertion that these processes are also likely to occur efficiently as radiative processes at cold cloud temperatures. In any event, the qualitative effects of reactions of $Fe^+ + C_mH_n$ upon dense cloud chemical evolution are expected to remain similar even if the rate coefficients for radiative association differ by, say, an order of magnitue from those suggested in this work.

2.2. *Effect of Primary Addition Reactions*

The primary addition reactions we consider are those of the type

$$Fe^+ + C_mH_n \rightarrow FeC_mH_n^+ + h\nu , \quad (4)$$

where C_mH_n is one of the known or likely interstellar hydrocarbons CH_4, C_2H_2, C_2H_4, CH_3CCH, and C_4H_2. In Table 1, we show a comparison between the estimated rates of reactions of type (4) and of (2) and (3) using the model of Millar et al. (1991) for abundances of reactants.

It is apparent from a perusal of Table 1 that the rates of removal of Fe^+ by reaction with C_2H_2 or with C_4H_2 exceed greatly the rate by which Fe^+ is neutralized by reactions (2) or (3). Therefore, ion/molecule reactions of Fe^+ are expected to represent the dominant loss process for this ion. If we consider a reaction network encompassing reactions (1)–(3), (5) and (6),

$$Fe^+ + C_2H_2 \rightarrow FeC_2H_2^+ + h\nu \,, \tag{5}$$

$$Fe^+ + C_4H_2 \rightarrow FeC_4H_2^+ + h\nu \,, \tag{6}$$

then the steady state abundance of Fe^+ can be expressed as

$$n(Fe^+) = \frac{k_1 n(X^+) n(Fe)}{k_2\, n(Na) + \alpha_3\, n(e) + k_5\, n(C_2H_2) + k_6\, n(C_4H_2)} \,. \tag{7}$$

Solution of this equation is necessarily an iterative process: $n(Fe^+)$ depends on $n(Fe)$ and vice versa. If we make the simplifying assumption that all gas-phase iron is in the form only of Fe or Fe^+, the early-time abundances in the model of Millar et al. (1991) can be used to derive an upper limit to $n(Fe^+)$. Using averaged values of $k_1 = 3 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} and $n(X^+) = 8.5 \times 10^{-9} n(H_2)$ for the occurrence of charge transfer reaction (1) for abundant interstellar ions X^+, we derive $n(Fe^+) = 6.25 \times 10^{-10} n(H_2)$. This is perhaps more usefully expressed in terms of the ratio $n(Fe^+){:}n(Fe) = 0.12$, which can be compared with a value of $n(Fe^+){:}n(Fe) = 10.2$ in the model of Millar et al. (1991). Clearly, the inclusion of Fe^+/hydrocarbon association reactions has reduced severely the abundance of Fe^+ that is to be expected within quiescent dark clouds. It should be noted also that substantial abundances exist of other species—for example, nitriles and hydrocarbon radicals—with which Fe^+ might be expected to undergo radiative association. Inclusion of these other classes of association reaction (which have not yet been studied experimentally) can only reduce $n(Fe^+)$ further. We caution, also, that the measurements detailed in Table 1 provide only an upper limit to the rate coefficient for reaction of Fe^+ with H_2, and we cannot exclude the possibility that this association may dominate all other Fe^+ association reactions under interstellar cloud conditions, although we consider this to be somewhat unlikely, given the very low radiative association rate coefficient, $k_{rad} = 4.4 \times 10^{-19}$ cm^3 molecule^{-1} s^{-1}, which Smith et al. (1983) have deduced for the analogous reaction of Na^+ at 20 K.

TABLE 1

ESTIMATED RELATIVE REACTION RATES OF Fe^+ WITH DENSE-CLOUD SPECIES

Species	$n(X)$[a]	k[b]	$kn(X)$[c]
CH_4	9.7 (+4)	5 (−4)	49
C_2H_2	1.2 (+4)	0.61	7320
C_2H_4	610	0.6	360
CH_3CCH	43	7.0	300
C_4H_2	4.2 (+3)	3.5	1.45 (+4)
Total hydrocarbons	...	...	2.25 (+4)
CO	8.5 (+5)	<1 (−4)[d]	"0"
H_2	1.0 (+10)	<2 (−4)[d]	"0"
e	270[e]	0.34	91
Na	3.5	0.1	0.35

[a] Abundance of species indicated. Abundances are expressed in units of $1 \times 10^{-10} n(H_2)$ and are taken from the UMIST ratefile calculations of Millar et al. 1991, unless otherwise indicated.

[b] Calculated or assumed bimolecular reaction rate coefficient, in units of 1×10^{-10} cm^3 molecule^{-1} s^{-1}, for the reaction indicated. All reactions of Fe^+ with hydrocarbons are observed to occur as addition processes.

[c] Relative rate of the indicated reaction, obtained as the product of the reactant abundance and the rate coefficient.

[d] Measured by Baranov et al. 1996.

[e] Adjusted free-electron abundance, obtained as described in § 2.2.

As we have already discussed qualitatively, inclusion of Fe^+/hydrocarbon association reactions also has a marked effect on the overall degree of ionization. The substantial reduction in the expected abundance of Fe^+ is coupled with a reduction in $n(e)$ from $3.15 \times 10^{-8} n(H_2)$ (Millar et al. 1991) to $2.67 \times 10^{-8} n(H_2)$ in the present model—a decrease of 15%.

2.3. *Effect of Secondary Addition Reactions*

The $FeC_mH_n^+$ ions produced via reaction (4) will also undergo further reactions under dense-cloud conditions. Since these ions are molecular rather than atomic, their neutralization by free electrons will be dissociative rather than radiative in nature: for example,

$$FeC_mH_n^+ + e \rightarrow Fe + C_mH_n \,, \tag{8a}$$

$$\rightarrow FeC_mH_{n-1} + H \,. \tag{8b}$$

In competition with reaction (8), further radiative association reactions are also possible, and we have reported the termolecular processes equivalent to such secondary radiative association reactions to be of comparable efficiency to the primary association reactions discussed in § 2.2 (Becker 1995). A difficulty in the analysis of secondary association reactions in the interstellar context is the resultant proliferation of pathways of the type

$$FeX^+ + Y \rightarrow [FeXY]^+ + h\nu \,, \tag{9}$$

where X and Y are different hydrocarbons. To date, our experimental studies have involved only those examples in which $X = Y$, and in these instances the reactions of $FeC_2H_2^+$ with C_2H_2 and of $FeC_4H_2^+$ with C_4H_2 are of more interstellar significance than other such reactions. In Table 2, we have presented some examples of reaction (9) with important IS hydrocarbons.

It should be noted that, while radiative recombination is an inefficient loss process for Fe^+, dissociative recombination is expected to be extremely efficient as a means of neutralizing FeX^+. Thus, as is borne out by the values calculated in Table 2, the association reactions of type (9) do not dominate the reaction chemistry of FeX^+ in the same manner as do reactions of type (4) for the Fe^+ chemistry.

A further difficulty in the modeling of association reactions of FeX^+ is that some species that do not appear to add measurably to Fe^+ are likely to add to the larger species FeX^+, which possesses more modes for randomization of internal energy and hence would have a longer collision complex lifetime. Important reactants in this respect include CO and H_2:

$$FeX^+ + CO \rightarrow Fe(X)CO^+ + h\nu \,, \tag{10}$$

TABLE 2

COMPARISON OF REACTION RATES OF Fe-CONTAINING ADDUCT IONS WITH DENSE-CLOUD SPECIES

Ion	Reactant	$n(X)$[a]	k[b]	$kn(X)$[c]
		Primary Adducts		
$FeC_2H_2^+$	C_2H_2	1.2 (+4)	7.7	9.3 (+4)
	CO	8.5 (+5)	0.57	4.8 (+5)
	H_2	1.0 (+10)	<5 (−3)	"0"
$FeC_2H_4^+$	C_2H_4	610	6.3	3.8 (+3)
	CO	8.5 (+5)	0.54	4.6 (+5)
$FeC_3H_4^+$	CH_3CCH	43	7.5	320
$FeC_4H_2^+$	C_4H_2	4.2 (+3)	10	4.2 (+4)
		Higher Adducts		
$Fe(C_2H_2)_2^+$	C_2H_2	1.2 (+4)	7.6	9.1 (+4)
	CO	8.5 (+5)	0.71	6.0 (+5)
$Fe(C_2H_2)_3^+$	C_2H_2	1.2 (+4)	0.018	2.2 (+2)
	CO	8.5 (+5)	2.1	1.9 (+6)
	H_2	1.0 (+10)	7.3 (−3)	7.3 (+7)
$Fe(C_2H_4)_2^+$	C_2H_4	610	0.87	530
$Fe(C_3H_4)_2^+$	CH_3CCH	43	6.0	260
$Fe(C_4H_2)_2^+$	C_4H_2	4.2 (+3)	3.0	1.3 (+4)
		All adducts		
FeX^+	e[d]	270[e]	5 (+3)	1.3 (+6)

[a] Abundance of species indicated. Abundances are expressed in units of $1 \times 10^{-10} n(H_2)$ and are taken from the UMIST ratefile calculations of Millar et al. 1991, unless otherwise indicated.

[b] Calculated or assumed bimolecular reaction rate coefficient, in units of 1×10^{-10} cm^3 molecule^{-1} s^{-1}, for the reaction indicated. All reactions of Fe^+ with hydrocarbons and with CO are observed to occur as addition processes.

[c] Relative rate of the indicated reaction, obtained as the product of the reactant abundance and the rate coefficient.

[d] We assume a dissociative recombination reaction rate independent of the nature of the hydrocarbon moiety X in FeX^+.

[e] Adjusted free-electron abundance, obtained as described in § 2.2.

$$FeX^+ + H_2 \rightarrow Fe(X)H_2^+ + h\nu \ . \qquad (11)$$

We have studied a few representative examples of the reactions (10) and (11) as shown in Table 2 as with the other reactions studied, we have assumed that the bimolecular rate coefficient for these reactions, under dense interstellar cloud conditions, is equal to the effective bimolecular rate coefficient observed for the (presumably termolecular) process under our experimental conditions. The observation of CO addition to FeX^+ is significant: CO does not add measurably to Fe^+, and, given the very high abundance of CO within interstellar clouds, this suggests that the addition of CO is likely to dominate over further addition of hydrocarbons to FeX^+. Another significant aspect of reaction (10) is that it appears to compete reasonably efficiently with dissociative recombination (8) as a loss process for FeX^+: we will discuss further implications of this competition in the next section. In contrast, H_2 does not add measurably to either Fe^+ or to single-adduct FeX^+ in the examples studied to date.

If reactions (8), (9), and (10) are the most important loss processes for FeX^+, then the pseudo–steady state expression for $n(FeC_mH_n^+)$ is

$$n(FeC_mH_n^+) = \frac{k_4\, n(Fe^+) n(C_nH_m)}{\alpha_8 n(e) + k_9\, n(Y) + k_{10}\, n(CO)} \ . \qquad (12)$$

This expression can be solved using the parameters specified above or contained within Millar et al. (1991), if the following additional assumptions are made. First, since the rate coefficients observed for CO addition to the primary adducts $FeC_2H_2^+$ and $FeC_2H_4^+$ are virtually identical, the rate coefficient for reaction (10) is considered to be independent of the nature of X. Second, in the absence of any information on the variation in reaction rate for reaction (9) with varying hydrocarbons Y, we consider that k_9 is independent of the nature of Y (though it does, clearly, depend upon X, as can be seen by the data in Table 2). These assumptions are made solely for reasons of computational simplicity in solving expression (12), and they may very well not hold in actuality. We have listed the $FeC_mH_n^+$ abundances thus obtained in Table 3.

The values displayed in Table 3 indicate that the expected abundances for $FeC_mH_n^+$ ions within dense interstellar clouds are substantially lower than $n(Fe^+)$, in accordance with the much greater rate for electron recombination expected for the molecular $FeC_mH_n^+$ ions. Of the adducts considered, $FeC_4H_2^+$ has the highest calculated abundance and therefore appears to be the most feasible candidate for interstellar detection; however, at an abundance of $\sim 4.7 \times 10^{-12} n(H_2)$, detection does not appear probable. We note that reaction (10), if efficient under interstellar conditions, is likely to be the dominant ion molecule loss process for $FeC_mH_n^+$ (although dissociative recombination [8] is the most important overall loss process). We caution also that the values calculated in this section are highly speculative, due to the number of assumptions that have been made in deriving the present chemical model: abundances for $FeC_mH_n^+$ are best regarded as guidelines only. We have not, for example, included any consideration of the addition reactions of FeX^+ with other prominent interstellar molecules such as HCN, H_2O, NH_3, or N_2: such reactions are also worth investigation but, unless exceedingly rapid, they are unlikely to dominate over reactions (8) or (10). In any event, since the dissociative recombination of $FeC_mH_n^+$ is almost certainly rapid, the values determined here would appear to represent fairly reliable upper limits for $n(FeC_mH_n^+)$ under typical dense-cloud conditions.

2.4. *Possible* Fe-*containing Molecular Products of Dissociative Recombination*

The likelihood of rapid dissociative recombination of Fe-containing molecular ions raises the possibility of formation of organometallic products. Two classes of process (at least) can be envisaged, involving, respectively, the dissociative recombination of primary and secondary adducts.

TABLE 3

CALCULATED ABUNDANCES OF $FeC_mH_n^+$ IONS AND FeC_mH_{n-1} NEUTRALS UNDER TYPICAL DENSE CLOUD CONDITIONS

		$n(FeC_mH_{n-1})$[a]	
C_mH_n	$n(FeC_mH_n^+)$[a]	$f_{8b} = 0.5$[b]	$f_{8b} = 0.1$[b]
C_2H_2	2.36 (−12)	1.58 (−10)	3.15 (−11)
C_2H_4	1.20 (−13)	8.01 (−12)	1.60 (−12)
CH_3CCH......	9.73 (−14)	6.49 (−12)	1.30 (−12)
C_4H_2	4.65 (−12)	3.10 (−10)	6.21 (−11)

NOTE.—The assumptions employed in modeling these abundances are detailed within the text.

[a] Pseudo–steady state abundance expressed as a fraction of the hydrogen abundance $n(H_2)$. Here $a(b) = a \times 10^b$.

[b] Assumed branching ratio for product channel (8b), as identified and discussed within the text.

2.4.1. *Recombination of Primary Adducts*

Dissociative recombination of primary adducts may involve competition between cleavage of an Fe—C and of a C—H bond, ie.,

$$FeC_mH_n^+ + e \rightarrow Fe + C_mH_n\ , \qquad (8a)$$

$$\rightarrow FeC_mH_{n-1} + H\ . \qquad (8b)$$

It is quite possible, especially since the positive charge on $FeC_mH_n^+$ can be considered as being substantially localized upon Fe (see, for example, Sodupe & Bauschlicher 1991), that channel (8a) dominates over any other possible product channels, in which instance the addition of C_mH_n has served mainly to catalyze the neutralization of Fe^+ and hence reduce the interstellar cloud's degree of ionization. However, if channel (8b) does occur to some extent, reaction (8) can also provide a pathway to neutral Fe-containing molecules.

A simplistic model for the reaction chemistry of FeC_mH_{n-1} neutrals is that they arise solely via reaction (8) and are destroyed only via reaction with energetic ions Z^+,

$$Z^+ + FeC_mH_{n-1} \rightarrow Z + Fe^+ + C_mH_{n-1}\ , \qquad (13)$$

where Z^+ includes species like H^+, He^+, and C^+, which presumably can break the Fe—C bond as well as transferring a charge to Fe. For this model, the steady state abundance of FeC_mH_{n-1} is

$$n(FeC_mH_{n-1}) = \frac{f_{8b}\,\alpha_8\, n(FeC_nH_m^+)n(e)}{k_{13}\, n(Z^+)}\ , \qquad (14)$$

where f_{8b} is the branching ratio for product channel (8b). We consider the abundances derived for two cases, $f_{8b} = 0.5$ and $f_{8b} = 0.1$. We have used, also, the values $n(Z^+) = 1 \times 10^{-8}\, n(H_2)$ and $k_{13} = 1 \times 10^{-8}$ cm^3 molecule^{-1} s^{-1} (both these values being likely upper limits) to derive the abundances shown in Table 3. It should be stressed, as before, that these values are highly speculative. However, the values do suggest that FeC_2H and FeC_4H may be present in sufficient abundance to permit their detection within a cloud such as TMC-1.

We note that the dissociative recombination (8) of $FeC_3H_4^+$ and $FeC_4H_2^+$ may also include a C—C single bond scission yielding, respectively, $FeC_2H + CH_3$ and $FeC_2H + C_2H$. For reasons of simplicity, we have not included this pathway in the model calculations discussed above: obviously, if such a channel were a significant pathway in the recombination of $FeC_3H_4^+$ or $FeC_4H_2^+$, it would raise the expected abundance of FeC_2H and improve the prospects for detection of this species.

2.4.2. *Recomination of Secondary Adducts*

The second type of process that we will consider is that of neutralization of secondary adducts. Our calculations in § 2.3 suggest that the only secondary adduct formation process to compete significantly with reaction (8) is the reaction of $FeC_mH_n^+$ with CO: therefore, we will speculate only on the possibilities for the dissociative recombination of the product of reaction (10), $[FeC_mH_nCO]^+$:

$$[Fe.C_mH_n.CO]^+ + e \rightarrow FeC_mH_n + CO\ , \qquad (15a)$$

$$\rightarrow FeCO + C_mH_n\ , \qquad (15b)$$

$$\rightarrow Fe + C_mH_n + CO\ . \qquad (15c)$$

Again, since charge localization upon the central metal atom is likely, dissociative recombination is likely to involve cleavage of a Fe-ligand bond. However, since the ion $[Fe.C_mH_n.CO]^+$ is two-coordinate, some retention of Fe within a molecular product appears likely as indicated in product channels (15a) and (15b). We have not attempted to estimate the abundances of neutral products of reaction (15) because of the large number of assumptions involved in modeling this process.

We note that the rotational spectrum of FeCO has been assigned recently by Kasai et al. (1995), permitting a preliminary (unsuccessful) search for this species within several sources. If FeCO is detected within TMC-1 or other sources, it is much more likely to arise via an indirect process such as reaction (10) than via the (very inefficient) process of radiative association of Fe^+ with CO.

2.5. *Ligand Switching Reactions*

In the preceding discussion, we have not considered any implications of the occurrence of ligand switching reactions such as

$$[Fe.C_4H_2.CO]^+ + C_2H_2 \rightarrow [Fe.C_4H_2.C_2H_2]^+ + CO\ , \qquad (16)$$

although many such reactions are certainly energetically feasible and are likely to compete efficiently with radiative association in many instances. Indeed, the formation of gas-phase hydrocarbon-containing Fe^+ adducts in various experimental studies has often been effected by ligand switching reactions of $Fe(CO)_n^+$ with hydrocarbons (Larsen & Ridge 1984; Peake, Gross, & Ridge 1984; Peake & Gross 1986). In the interstellar context, where CO is the most abundant molecule likely to react with Fe-containing ions, replacement of hydrocarbon ligands by CO may (if exothermic) compete with further association reactions (10): the thermochemistry of Fe^+/hydrocarbon adducts is still rather uncertain, so it is not yet possible to determine whether reaction (16), for example, is exothermic or endothermic. Switching of hydrocarbon ligands by CO would act to interrupt the pathways leading to neutral FeC_mH_{n-1} and FeC_mH_n: we note that no switching was observed under our SIFT conditions (0.35 torr of helium, 294 K) in the instance

$$FeC_2H_2^+ + CO \rightarrow [Fe.C_2H_2.CO]^+\ , \qquad (17)$$

suggesting that, in this case at least, switching should not interfere with the competing association channel under interstellar cloud conditions.

A related concept is that of ligand-switching reactions involving interstellar radicals. Within dense interstellar clouds, the most abundant radicals are generally considered to be the free atoms H, C, and O. Few data exist on the participation of such species in ligand switching, but Mestdagh et al. (1992) have noted the occurrence of the reaction

$$FeCO^+ + H \rightarrow FeH^+ + CO\ , \qquad (18)$$

in a triple-quadrupole mass spectrometer. Reaction (18) is estimated to be exothermic by ~40 kJ mol^{-1}. The analogous reaction of a generic Fe^+/hydrocarbon adduct

$$FeC_mH_n^+ + H \rightarrow FeH^+ + C_mH_n\ , \qquad (19)$$

is very likely also exothermic and may be efficient under interstellar cloud conditions: if this is so, then at a typical abundance $n(H) \sim 1 \times 10^{-5} n(H_2)$ and with an estimated rate coefficient $k_{19} \sim 1 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} for reaction upon every collision, reaction (19) is of comparable efficiency to the dissociative recombination reaction (8) as a loss process for $FeC_mH_n^+$. If reaction (19) is indeed rapid, it will act to reduce the expected abundances of any Fe-containing molecules derived from ion/molecule reactions, for at least two reasons. First, FeH^+ is most likely to be removed by dissociative recombination, yielding only the atomic products Fe + H. Second, as we have discussed above, the prospects for Fe-molecule formation upon dissociative recombination are substantially better for secondary and higher order adducts than for the primary adducts of the type $FeC_mH_n^+$. It is very likely that formation of secondary adducts by radiative association reactions of FeH^+,

$$FeH^+ + C_mH_n \rightarrow [Fe.H.C_mH_n]^+ + h\nu , \quad (20)$$

will be substantially less efficient than the analogous reaction

$$FeC_jH_k^+ + C_mH_n \rightarrow [Fe.C_jH_k.C_mH_n]^+ + h\nu , \quad (21)$$

involving a hydrocarbon-bearing adduct $FeC_jH_k^+$. The collision complex lifetime for association depends (considerations of well depth aside) on the number of vibrational and rotational modes of freedom: FeH^+, possessing only one vibrational and two rotational modes, contributes very few degrees of freedom to the collision complex formed in reaction (20), while $FeC_jH_k^+$ possesses many more modes (for example, nine vibrational and three rotational modes for $FeC_2H_2^+$) and so the collision complex $[Fe.C_jH_k.C_mH_n]^+$ involved in reaction (21) should have a much longer lifetime than that featured in reaction (20), provided that the potential well depths for these two association reactions are comparable.

Notwithstanding the above discussion, it is quite possible that ligand-switching reactions, even if very efficient, may have very little impact upon the overall "observable" chemistry of Fe within interstellar clouds. As we have discussed in § 2.4, it is by no means certain that dissociative recombination of any Fe-containing ions will yield Fe-containing molecular products. We expect, also, that the rate coefficient for neutralization of any Fe-containing molecular ion will be large at interstellar cloud temperatures and insensitive to the structure of this ion: that is, the recombination coefficient for dissociative recombination of the diatomic ion FeH^+ should be similar to that for recombination of the polyatomic ions $FeC_jH_k^+$ and $[Fe.CH_k.C_mH_n]^+$. If, as we have suggested earlier, the most significant effect of Fe^+ association reactions is to reduce the abundance of gas-phase Fe^+ and to limit the overall degree of ionization, then ligand switching is of no real importance, since it will not affect these parameters greatly.

2.6. *General Discussion*

Clearly, a number of other Fe-containing ion/molecule reactions must be studied in order to obtain a full understanding of the chemical processing of iron within dense interstellar clouds. To this end, we have reported elsewhere (Baranov et al. 1996) upper limit for the nonreaction of Fe^+ with the interstellar cloud constituents H_2, CO, N_2, H_2O, O_2, CO_2, and NO; but several other neutrals may be important in this regard, such as NH_3, HCN, HC_3N, and many radical species such as C_2H, OH, and CN. In the absence of a more complete picture, we can still appreciate that the inclusion of Fe^+/hydrocarbon chemistry appears to have a substantial influence upon the disposition of iron-containing species within interstellar clouds. A schematic diagram of the proposed chemical evolution of iron in the gas phase is given in Figure 1.

A topic of considerable interest is the possible role of Fe^+ association reactions in the interstellar synthesis of PAHs. Mass spectrometric studies have demonstrated that some Fe^+/hydrocarbon reactions (Schröder et al. 1991; Bakhtiar, Drader, & Jacobson 1992; Bohme et al. 1996) occur as cyclizations: for example, the reaction

$$Fe(C_2H_2)_3^+ + C_2H_2 \rightarrow FeC_6H_6^+ + C_2H_2 , \quad (22)$$

could play a role in the interstellar synthesis of benzene. However, the probability of sequential triple addition of acetylene to Fe^+ within dense clouds is slight, given the far greater probability of reaction with an electron or with CO at any step. Thus, reactions of type (22) are unlikely to be important in the production of PAHs under typical dense-cloud conditions.

The reactions of Fe^+ with small PAHs—benzene, naphthalene, and anthracene—have been studied using the SIFT (Becker 1995), ion trap (Boissel 1994), and FT-ICR (Dunbar et al. 1994) techniques. The observation of association reactions, ultimately yielding $Fe(PAH)_2^+$ ions, in the low-pressure ion trap and FT-ICR experiments is compelling evidence for the occurrence of efficient radiative association at room temperature. This provides strong support for the notion that radiative association of Fe^+ with benzene, and with even smaller neutrals such as C_2H_2 and C_4H_2 in the present study, can occur with reasonable efficiency at cold cloud temperatures. The importance of Fe^+/PAH chemistry is difficult to assess given the current uncertainty in the abundances of PAHs within interstellar clouds. A very recent study (Klotz et al. 1995) has found a strong correlation between the binding energy of metal ions to typical PAHs and observed interstellar depletion for metallic elements, suggesting that reactions of metal ions such as Fe^+ with PAHs may play a part in the removal of these metals from the gas phase. Such a scheme may well be of significance within diffuse interstellar clouds; within denser regions, having a high abundance of unsaturated hydrocarbons such as C_2H_2 and C_4H_2, it would appear that the

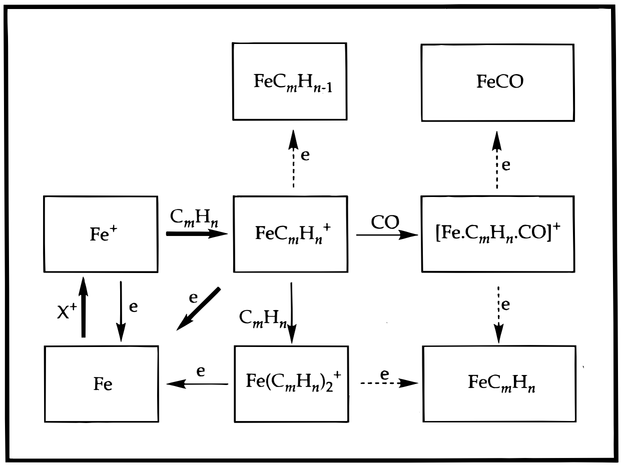

FIG. 1.—A simple reaction network detailing probable or possible reaction pathways for Fe^+ with hydrocarbons (principally C_2H_2 and C_4H_2) and with CO under dense interstellar cloud conditions. Speculative dissociative recombination pathways are indicated by arrows featuring dotted lines; major reaction pathways are shown by bold arrows.

rather low $n(Fe^+)/n(Fe)$ ratio (resulting from the chemistry outlined in § 2.2) will limit the importance of Fe^+/PAH reactions as a depletion mechanism.

Reactions of the positive ions of other abundant metals are also likely to be of significance. If association reactions of Mg^+, Ni^+, Ca^+, Al^+, Cr^+, Mn^+, and Ti^+ with abundant interstellar neutrals dominate over radiative recombination of these ions, a further reduction in the degree of ionization expected within clouds will result. In the models of Millar et al. (1991) and of Herbst & Leung (1986), only Mg has been considered of sufficient abundance to be included. We estimate, in the absence of any experimental measurements upon the efficiency of Mg^+/hydrocarbon association reactions, that a total decrease in the degree of ionization of around 30% will result if the conversion of atomic (Fe or Mg)$^+$ to (Fe or Mg)$^+$/hydrocarbon adducts is efficient under dense interstellar cloud conditions. The rapid conversion of Mg^+ to various adducts would imply, also, that the most abundant metal ion within dense interstellar clouds is Na^+, since this is the third most abundant metal ion in the previous model calculations (Herbst & Leung 1986; Millar et al. 1991), and since Na^+ does not appear to undergo efficient association reactions with abundant interstellar neutrals (Smith et al. 1983).

The effect of a reduction in the expected degree of ionization on models of cloud chemistry is not straightforward, and it is beyond the scope of the present work to investigate this issue fully. However, a comparison of the "low-metal" and "high-metal" models of Herbst & Leung (1989) suggests that a reduction in the abundance of free electrons should be accompanied by an increase in the extent of complex molecule formation. This is consistent with a reduction in the rate of occurrence of dissociative recombination compared to more "gentle" processes such as proton transfer as pathways for the removal of molecular ions.

Finally, it should be noted that many of the implications that we have outlined for the Fe^+ chemistry of interstellar clouds are applicable also to the chemical evolution of carbon-rich circumstellar envelopes (CSEs) such as that associated with the asymptotic giant branch (AGB) red giant IRC +10216. Several metal halides (Cernicharo & Guélin 1987; Ziurys, Apponi, & Phillips 1994) and metal cyanides (Kawaguchi et al. 1993; Turner, Steimle, & Meerts 1994; Ziurys et al. 1995) have been detected within the CSE surrounding IRC +10216: of these species, it has been proposed that the metal cyanides Na(CN), MgCN, and MgNC arise via metal-ion radiative association reactions with abundant neutrals (Kawaguchi et al. 1993; Petrie 1996). Detection of these metal-containing species within IRC +10216 suggests that such objects may possess higher gas-phase abundances of the refractory elements than is normally the case within dense interstellar clouds, and the abundances of highly unsaturated hydrocarbons (C_2H_2, C_4H_2, etc.) within IRC +10216 are also thought to be substantially higher than within interstellar clouds. These observations indicate also that CSEs may be better "hunting grounds" for Fe-containing molecules than the dense interstellar clouds. Some differences in the Fe^+ chemistry of CSEs and of dense interstellar clouds are likely, however, since CSEs are characterized by a comparatively short expansion timescale; photodissociation processes are also generally more important within CSEs than within the interiors of dense interstellar clouds. A detailed discussion of the likely role of Fe^+/hydrocarbon reactions within CSEs is beyond the scope of this study, although efforts to detect Fe-containing species within objects such as IRC +10216 are certainly recommended.

3. CONCLUSION

The efficient occurrence of Fe^+/hydrocarbon association reactions under cold interstellar cloud conditions is expected to have a profound effect on the ratio of neutral to ionized Fe-containing species within the gas phase. Such reactions are also expected to reduce significantly the abundance of free electrons within dense interstellar clouds, by virtue of the much greater rate expected for dissociative recombination of Fe-containing molecular ions than for the radiative recombination of Fe^+.

If dissociative recombination of $FeC_nH_m^+$ ions occurs without always breaking the Fe—C bond, then the neutrals FeC_2H and FeC_4H may be present in sufficient abundance within dense clouds such as TMC-1 to permit their detection. Other neutrals such as FeCO, FeC_2H_2, and FeC_4H_2 are possible products of the dissociative recombination of Fe-containing secondary adduct ions.

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