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DIFFUSE INTERSTELLAR CLOUDS AS A CHEMICAL LABORATORY: THE CHEMISTRY OF DIATOMIC CARBON SPECIES

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ABSTRACT

The chemistry of C_2, CH, and CO in diffuse interstellar clouds has been analyzed and has been compared to absorption line measurements toward background stars. Analytical expressions in terms of column densities have been derived for the rate equations. Observed column densities for the progenitor molecules have been used as input in the equations so that isolated parts of the chemical network could be studied. The modifications introduced through the analysis of one of the molecules have been shown to apply equally well to the other species.

The analysis leads to several modifications in the chemistry. In clouds with 4 mag of visual extinction, the abundance of C^+ has to decrease by a factor of ~ 15 from the value traditionally used for clouds with 1 mag of extinction. The rate coefficients for the reactions $C^+ + CH \rightarrow C_2^+ + H$ and $C^+ + H_2 \rightarrow CH_2^+ + h\nu$ need to be reduced from previous estimates. Chemical arguments are offered for the revised rate coefficients. Moreover, the primary cosmic-ray ionization rate in clouds with $A_V \sim 4$ mag is approximately 2–8 $\times 10^{-17}$ s^{-1}, somewhat lower than estimates for clouds with $A_V \sim 1$ mag.

Subject headings: interstellar: abundances — interstellar: molecules — molecular processes

I. BACKGROUND AND INTRODUCTION

Two complementary approaches have been applied to the analysis of absorption line measurements for diffuse clouds. One approach utilizes an extensive set of data for a particular line of sight in order to deduce the physical conditions, such as density, temperature, and radiation field, and the chemical schemes appropriate to the cloud. Examples of this approach include the studies by Black and Dalgarno (1977), Federman and Glassgold (1980), van Dishoeck and Black (1986), and Viala, Roueff, and Abgrall (1988). The other approach places the emphasis on observations of one molecule toward many directions; the trends seen in the data are used to place constraints on the underlying chemical foundation in *all* diffuse clouds. The latter approach often incorporates results for physical conditions in specific clouds so that the number of unknown quantities is restricted. Federman, Danks, and Lambert (1984) and Federman and Lambert (1988) have examined the chemistry of CN via this ensemble approach. The present work on C_2, CH, and CO is a continuation of our applying the ensemble approach to the study of interstellar chemistry.

A goal in this approach is to discern persistent deviations from anticipated trends. In order to define these deviations, "standard" values for certain parameters, such as the ultraviolet flux impinging on the cloud, are held constant. The causes of the persistent deviations often reveal necessary modifications to the chemistry, including changes in rate coefficients for reactions that have not been measured in the laboratory. On the other hand, a deviation from predictions in the study of the detailed chemistry of a specific sight line may arise from a larger set of possible revisions.

Federman, Danks, and Lambert (1984) studied the chemistry of CN by comparing observations with an analytical expression for the rate equation of this molecule. The novel feature of their method is the incorporation of the *observed* column densities of progenitor species into the rate equation. For the case of CN, the column densities of CH and C_2, N(CH) and $N(C_2)$, are used in the analysis to derive N(CN). Federman and Lambert (1988) showed that this method is applicable to the chemistry of CN not only in lines of sight that sample gas undergoing predominantly photochemical reactions but also in lines of sight where particle collisions dominate the chemistry. In this paper, we extend the method by studying the chemistries of C_2, CH, and CO in clouds with 1–4 mag of visual extinction. Our analyses indicate that the method is useful in elucidating key aspects of the chemistry, including fractional abundances and rate coefficients.

The technique relies on isolating the chemistry of a molecule in terms of the most important production and destruction pathways. The column density of the species in question is obtained by equating production to destruction—the steady-state approximation. The production is written as the product of rate coefficients and *observed* column densities of progenitor molecules. The use of observed column densities eliminates uncertainties arising from other parts of the larger chemical network.

The justification for solving from column densities, when rate equations are more appropriately derived from local conditions, requires comment. A continuous increase in the local density of species X, $n(X)$, with depth into a cloud leads to a corresponding increase with depth for the column density, $N(X)$, and thus to similar distributions for $n(X)$ and $N(X)$. Conversely, if the peak in the distribution for $n(X)$ lies outside the cloud core, the distributions for $n(X)$ and $N(X)$ may differ. For the diatomic molecules studied by us, appropriate case studies that bear on the question of distribution are hydrostatic models for the chemistry in molecular clouds (de Jong, Dalgarno, and Boland 1980; Boland and de Jong 1984). These models produce distributions in $n(X)$ that increase *logarithmically* as a function of A_V (or depth into the cloud) for $A_V \leq 2$ mag. These results are applicable to our analysis for lines of sight with total extinction less than or equal to 4 mag. We utilize data from absorption lines, which sample all the gas along the line of sight to a star, including the core of the cloud. Because of the logarithmic nature of the distributions, observations preferentially sample the core region, and the equivalence of local densities and column densities in the analysis is a reasonable approximation.

The remainder of the paper is organized in the following manner. The chemistry of C_2 is analyzed in § II. In order to reproduce the observations, we require the abundance of C^+ to decrease in a linear manner by a factor of ~ 15 in clouds with visual extinction of ~ 1 mag to ~ 4 mag. We also require the rate coefficient for the reaction $C^+ + CH \rightarrow C_2^+ + H$ to be substantially smaller than the Langevin rate coefficient. Federman and Lambert (1988) first noticed the need for lower values of $x(C^+)$; here, through a more comprehensive treatment of the C_2 chemistry, we quantify the reasons for the decrease and discuss its effect on other aspects of the chemistry. In § III, these findings are applied to measurements of CH and CO. Good agreement between the observations and the analytical calculations are obtained. For moderately reddened directions ($A_V \rightarrow 4$ mag), the results for CO indicate a cosmic-ray ionization rate of 2–8 $\times 10^{-17}$ s^{-1}. The final section § IV includes a discussion of our results, as well as our conclusions.

II. C_2 CHEMISTRY

The production of molecular carbon is initiated by reactions between C^+ and CH, followed by a series of hydrogen-atom abstraction reactions and finally dissociative electron recombination of the hydride ions (Watson 1974). Some production arises from the photodissociation of C_2H. The specific reactions are

$$C^+ + CH \rightarrow C_2^+ + H\ , \tag{1a}$$

$$C_2^+ + H_2 \rightarrow C_2H^+ + H\ , \tag{1b}$$

$$C_2H^+ + H_2 \rightarrow C_2H_2^+ + H\ , \tag{1c}$$

$$C_2H^+ + e^- \rightarrow C_2 + H\ , \tag{1d}$$

$$C_2H_2^+ + e^- \rightarrow C_2 + 2H\ , \tag{1e}$$

and

$$C_2H + h\nu \rightarrow C_2 + H\ . \tag{1f}$$

Experimental data exist for reactions (1b) and (1c) (see Anicich and Huntress 1986) and for the reactions (1d) and (1e) involving electron recombination (Mul and McGowan 1980), but in the steady-state approximation these intermediate steps, including (1f), cancel in the rate equation for C_2. The branching ratio between the formation of C_2 and C_2H for reaction (1e) introduces a constant of order unity into the rate equation.

The steady-state rate equation for C_2 can be written in terms of the initiating production process and three destruction mechanisms. These destruction mechanisms are photodissociation and neutral-neutral reactions with atomic oxygen and atomic nitrogen (see Federman and Lambert 1988). The equation for $N(C_2)$ is

$$N(C_2) = \frac{k_3\, n(C^+) N(CH)}{G(C_2) + k' n(O) + k_8\, n(N)}\ \text{cm}^{-2}. \tag{2}$$

Here, $n(X)$ equals the fractional abundance relative to protons of species X multiplied by the local gas density, $n(H) + 2n(H_2)$; the rate coefficients for the reactions (1a), $C_2 + O \rightarrow CO + C$, and $C_2 + N \rightarrow CN + C$ are, respectively, k_3, k', and k_8; and $G(C_2)$ is the photodissociation rate of C_2. The attenuation of the incident ultraviolet radiation by grains is treated, as in our previous work, by incorporating the term exp $(-\tau_{uv})$, where τ_{uv} is taken to be $2A_V$. The correspondence between τ_{uv} and A_V is based on photometry obtained with the *OAO 2* satellite (Code *et al.* 1976). The values used for the rate coefficients and photodissociation rate are shown in Table 1. The fractional abundance of ionized carbon is 2.5×10^{-4}, but, as will be shown below, this value is not appropriate for all the directions studied by Federman and Lambert (1988). The abundances for atomic oxygen and atomic nitrogen are 3.5×10^{-4} (de Boer 1979) and 6.9×10^{-5} (Hibbert, Dufton, and Keenan 1985).

When densities and kinetic temperatures are taken from analyses of H_2 and C_2 excitation, as well as chemical considerations (e.g., van Dishoeck and Black 1986), the results for N(CN) of Federman and Lambert (1988) indicate that the

TABLE 1

PRODUCTION AND DESTRUCTION MECHANISMS

Molecule	Mechanism	Reaction	Rate Coeff./Rate (cm^3 s^{-1} or s^{-1})	Notes
C_2	Production	$C^+ + CH \rightarrow C_2^+ + H$	1×10^{-9}	a
			3×10^{-10}	b
	Destruction	$C_2 + h\nu \rightarrow 2C$	2×10^{-10}	c
		$C_2 + O \rightarrow CO + C$	4×10^{-11}	a, d
		$C_2 + N \rightarrow CN + C$	5×10^{-11}	a, d
CH	Production	$C^+ + H_2 \rightarrow CH_2^+ + h\nu$	5×10^{-16}	e
			1×10^{-16}	b
	Destruction	$CH + h\nu \rightarrow C + H$	1.3×10^{-9}	f
		$C^+ + CH \rightarrow C_2^+ + H$	$2\text{–}3 \times 10^{-10}$	b
		$CH + O \rightarrow CO + H$	9.5×10^{-11}	d, g
CO	Production	$C^+ + OH \rightarrow CO^+ + H$	2.9×10^{-9}	a
		$CH + O \rightarrow CO + H$	9.5×10^{-11}	d, g
		$C_2 + O \rightarrow CO + C$	4×10^{-11}	a, d
	Destruction	$CO + h\nu \rightarrow C + O$	See text	h
		$He^+ + CO \rightarrow He + C^+ + O$	1.6×10^{-9}	i

NOTES.—(a) Estimate; (b) Derived in this work; (c) Pouilly *et al.* 1983, corrected for appropriate radiation field (van Dishoeck 1987*b*); (d) Rate coefficient has a temperature dependence of $(T/300)^{0.5}$; (e) Herbst, Schubert, and Certain 1977; (f) Barsuhn and Nesbit 1978; (g) Messing *et al.* 1981; (h) Included the effects of self-shielding; (i) Anicich and Huntress 1986.

TABLE 2

RESULTS FOR C_2

Star (1)	Pred/Obs N(CN) (2)	N(CH) (cm^{-2}) (3)	$N(C_2)$ (cm^{-2}) obs (4)	pred (5)	Pred/Obs $N(C_2)$ (6)[a]	(7)[b]
o Per	0.5	1.3 (13)[c]	2.7 (13)	4.7 (13)	1.7	1.7
ζ Per	0.4	2.2 (13)	3.5 (13)	7.9 (13)	2.3	2.0
X Per	2.0	3.1 (13)	5.3 (13)	8.4 (14)	16.	2.6
HD 29647	0.7	1.6 (14)	1.5 (14)	1.2 (16)	80.	5.6
HD 147889	2.5	1.2 (14)	1.2 (14)	5.8 (15)	48.	3.4
ρ Oph A	1.7	2.4 (13)	2.6 (13)	2.1 (14)	8.1	2.3
χ Oph	5.0	3.4 (13)	3.5 (13)	3.4 (14)	9.7	2.1
ζ Oph	0.6	2.5 (13)	2.2 (13)	1.4 (14)	6.4	6.4
HD 154368	1.1	8.7 (13)	5.1 (13)	3.0 (15)	59.	5.6
HD 206267	1.0	2.6 (13)	7.6 (13)	2.8 (14)	3.7	0.9
HD 207198	1.7	4.5 (13)	3.0 (13)	7.3 (14)	24.	4.0
λ Cep	1.7	2.2 (13)	1.7 (13)	2.9 (14)	17.	3.3

[a] No correction for decreasing $x(C^+)$.

[b] Correction for $x(C^+)$ between 1 mag and 4 mag.

[c] 1.3 (13) = 1.3×10^{13}.

analytic approach reproduces the observations within a factor of 2 or 3. This fact is made apparent in the second column of Table 2, where the ratio of the predicted column density to the observed one is displayed; the average value for the ratio is ~ 1, with variations about the average in the above stated range. Slight modifications to the model input parameters, such as higher ultraviolet fluxes or different densities and temperatures, would improve the correspondence, but these adjustments are not necessary when the general aspects of the chemistry are of interest.

A similar comparison for $N(C_2)$ also is presented in this table. Columns (3) and (4) display the observed values for N(CH) and $N(C_2)$, while column (5) shows the predicted values for $N(C_2)$ from equation (2) with the densities, temperatures, and the observed values for N(CH) from Federman and Lambert (1988). Column (6) displays the ratio of columns (5) to (4). For *each* of the lines of sight, the ratio for $N(C_2)$ is greater than 1 and, in some cases, significantly larger than 1.

The lines of sight with the largest deviation from prediction are also the most reddened. Figure 1 shows that there is a trend between the value for the ratio in column (6) of Table 2 and τ_{uv}, or equivalently A_V. As the opacity increases, the predictions of the calculations become progressively worse. No change in rate for the exothermic reaction (1a) is likely to be the cause of the trend. Neither are the destruction terms the cause, since photodissociation dominates at the smallest opacities, while the relatively rapid collisional reactions are more important at the largest opacities. The effect can be removed by a systematic

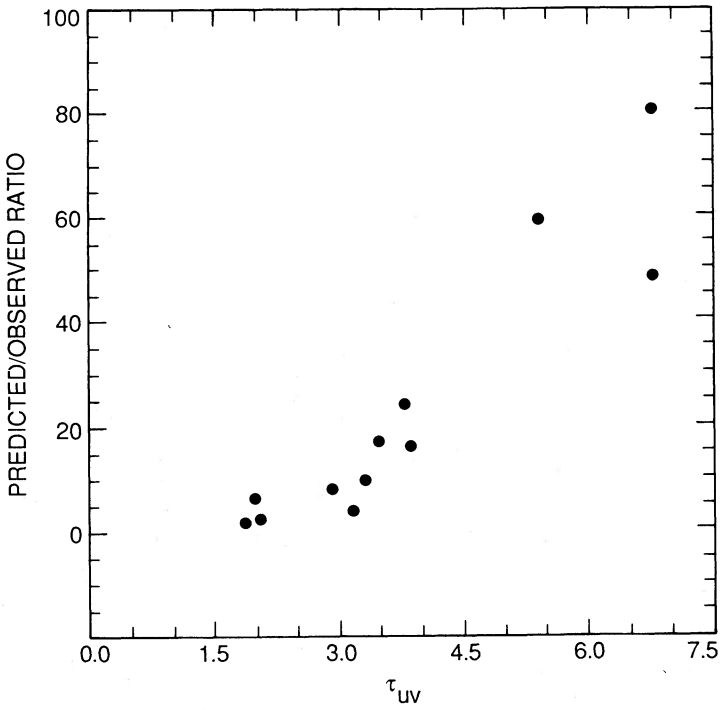

FIG. 1.—The ratio of predicted to observed column density for C_2 plotted against τ_{uv}. The ratios are from column (6) of Table 2.

linear decrease in the abundance of C^+, which appears as part of the production term for C_2. A factor of ~ 15 decrease in $x(C^+)$ is required to remove the slope from Figure 1.

A representative case for decreasing $x(C^+)$, which is based on the upturn at $\tau_{uv} \sim 2$ seen in Figure 1, is considered. It has the decrease occurring between 1 mag and 4 mag of visual extinction with an initial value of 2.5×10^{-4} for $x(C^+)$. An extra term in the rate equation that incorporates a linear decrease was included in a multiplicative way for this analysis. The results are presented in column (7) of Table 2. The ratio now attains an average value of ~ 3. There is no longer a slope in the ratio relative to τ_{uv}, but the average value does not vary about unity, indicating that another aspect of the C_2 chemistry requires modification.

The production term is again the likely place for modification; two destruction terms varying independently cannot easily account for a constant factor differing from unity. A value for k_3 of 3×10^{-10} cm^3 s^{-1}, instead of 10^{-9} cm^3 s^{-1}, can rectify the discrepancy between the observed and predicted column densities. In the absence of laboratory data on this reaction, we present a rationale for a rate coefficient less than traditionally used. There are four exothermic or thermoneutral channels for the reaction:

$$C^+ + CH \rightarrow \begin{cases} C_2{}^+ + H + 46 \text{ kcal mole}^{-1} & (3a) \\ CH^+ + C + 14 \text{ kcal mole}^{-1} & (3b) \\ C_2 + H^+ + 8 \text{ kcal mole}^{-1} & (3c) \\ C^+ + CH + 0 \text{ kcal mole}^{-1} \,. & (3d) \end{cases}$$

Reaction (3a) is the channel considered in many models of interstellar chemistry even though other channels, (3b)–(3d), are available. Black, Dalgarno, and Oppenheimer (1975), however, incorporated reaction (3b) in their study. There are no laboratory measurements for reaction (3), nor are there likely to be any measurements in the near future because of the difficulty of producing the CH radial under the appropriate laboratory conditions. We, therefore, take recourse to analogous processes to estimate the probability of branching for reaction (3) into each of the four channels.

Reaction (3c), if it were to occur, would produce C_2 directly. Reaction (3c), however, is of a type for which there are no precedents from laboratory data (Huntress 1977; Anicich and Huntress 1986). The only reactions in which protons are observed as products are charge transfer reactions, either direct transfer to H atoms as in the reaction involving CO^+ and H, or via dissociative charge transfer as in reactions between He^+ and H_2O. For any reaction where an alternate exothermic channel to proton elimination exists, the alternate seems to be highly favored. Such is the case with reaction (3), in which there are two channels more exothermic than (3c), each of a type commonly observed in the laboratory. Therefore, we eliminate reaction (3c) as a plausible candidate branch for reactions between C^+ and CH.

Reaction (3b), like reaction (3a), is of a type commonly observed for carbon ions. In almost every case examined in the laboratory where charge transfer involving C^+ is exothermic, the reaction is observed to some extent, even in the presence of alternate channels. Examination of the available data on reactions of C^+ (Anicich and Huntress 1986) shows that carbon atom insertion, in which a new C–C or C–X bond is formed (X is O, N, or S), is preferred and that the charge remains on the fragment containing the new bond. Reaction (3a) is just such a case; however, charge transfer accounts for 20%–30% of the product distribution for all those cases where the channel is exothermic. The only large exception is the reaction between C^+ and NO, where charge transfer is the exclusive exothermic channel. Therefore, reaction (3b) is a viable product channel, and given the available laboratory data on product distributions for charge transfer, we assign 30% of reaction (3) to channel (3b).

Reaction (3d) is formally equivalent to nonreactive scattering, but in this case exchange of the hydrogen atom takes place. The exchange occurs by H^- transfer from CH to C^+. Hydride ion transfer is a common reaction type for hydrocarbon ions and is often observed when exothermic. Hydride ion transfer has been observed to account for 15%–30% of the product distribution for reactions of C^+ with C_2H_4, C_2H_6, H_2CO, CH_3OH, and CH_3NH_2 (Anicich and Huntress 1986). For reactions of $CH_3{}^+$ with the same molecules, hydride ion transfer accounts for 40%–100% of the product distribution. Reaction (3d) is thermoneutral and must compete with other available exothermic channels, but there is no *a priori* reason why even in this case hydride ion transfer cannot be significant as a resonant, nonreactive scattering mechanism.

The Langevin rate coefficient between C^+ and CH, an improvement to the estimate in Table 1, has been determined from the average dipole orientation (ADO) theory of Su and Chesnavich (1982). The value for the rate coefficient is $\sim 2.7 \times 10^{-9}$ cm^3 s^{-1}, somewhat larger than that in Table 1. This fairly large value arises from the large dipole moment for CH: $\mu = 1.46$ debye. A value of $\sim 3 \times 10^{-10}$ cm^3 s^{-1} is required for channel (3a) from our analysis of the amount of C_2 in diffuse clouds. This would require a branching ratio of 60% for reaction (3d), a somewhat high but not unreasonable value given the large spread in the laboratory data for this process. The rate coefficients for the respective branches of reaction (3) then are 2.7×10^{-10} cm^3 s^{-1}, 8.1×10^{-10} cm^3 s^{-1}, 0, and 1.6×10^{-9} cm^3 s^{-1}.

Thus, the analysis of C_2 abundances has revealed two new modifications to the chemistry of this species. A decrease in the abundance of C^+ to approximately 1.7×10^{-5} in clouds with $A_V \sim 4$ mag is necessary, and the initiating reaction (1a) has a rate coefficient significantly less than the collisional rate coefficient. The chemistries of CH and CO are now analyzed in order to verify these results.

III. CONSEQUENCES

a) CH *Chemistry*

A linear relationship between $N(CH)$ and $N(H_2)$ was found by Federman (1982) and Federman, Danks, and Lambert (1984) for directions with $A_V \leq 1$ mag. Cardelli and Wallerstein (1986) showed that the relationship is also appropriate to optical observations of sight lines with A_V approaching 4 mag. The latter authors used the amount of reddening and the correspondence between $E(B-V)$ and $N(H_2)$ from Bohlin, Savage, and Drake (1978) to estimate $N(H_2)$. Moreover, the ratio of $N(CH)$ to $N(H_2)$ is constant for the available data. The present analysis of the CH chemistry, therefore, centers on this constant ratio.

The rate equation for CH in terms of $N(CH)/N(H_2)$ is

$$\frac{N(CH)}{N(H_2)} = \frac{0.67 k_5 n(C^+)}{G(CH) + k_3 n(C^+) + k_4 n(O)} \,. \tag{4}$$

The equation is similar to the one presented by Federman and Lambert (1988), with the addition of the destruction term

$k_4\,n(\mathrm{O})$. The reactions $\mathrm{CH} + \mathrm{O} \rightarrow \mathrm{CO} + \mathrm{H}$ and $\mathrm{C}^+ + \mathrm{H}_2 \rightarrow \mathrm{CH}_2{}^+ + h\nu$ have rate coefficients k_4 and k_5; the photodestruction rate for CH is $G(\mathrm{CH})$. Table 1 lists the values used for the rate coefficients and the photodestruction rate. The photodestruction rate of Barsuhn and Nesbit (1978) is used; the rate calculated recently by van Dishoeck (1987*a*) is quite similar to the one used here.

The observed value for the ratio is 3×10^{-8}. For directions with $A_V \sim 1$ mag, such as that toward ζ Oph or ζ Per, a simpler version of equation (4) is applicable because photochemical reactions dominate the destruction:

$$\frac{N(\mathrm{CH})}{N(\mathrm{H}_2)} \rightarrow \frac{0.67 k_5\, n(\mathrm{C}^+)}{G(\mathrm{CH})} . \tag{5}$$

With a gas density of ~ 400 cm^{-3} and a kinetic temperature of ~ 50 K (see van Dishoeck and Black 1986), the value for k_5 must be reduced to 1×10^{-16} cm^3 s^{-1} for reasonable agreement with the observed ratio. The theoretical value for the ratio then becomes 4×10^{-8}. The derived value for k_5 is consistent with the lowest values calculated by Herbst (1982) and the value deduced from analyzing the chemistry of dark clouds (Boland and de Jong 1984).

For directions with $A_V \sim 4$ mag, such as that toward HD 29647, a density of 1000 cm^{-3} and a temperature of 25 K are more appropriate (Crutcher 1985). Without decreasing the abundance of C^+ from 2.5×10^{-4}, but using the new values for k_3 and k_5, the ratio of $N(\mathrm{CH})$ to $N(\mathrm{H}_2)$ becomes

$$\frac{N(\mathrm{CH})}{N(\mathrm{H}_2)} \rightarrow \frac{0.67 k_5}{k_3} \sim 3 \times 10^{-7} , \tag{6}$$

which is too high. When $x(\mathrm{C}^+)$ is reduced by a factor of 15, the other destruction mechanisms shown in Table 1 have to be included and equation (4) is the appropriate expression to use. The application of all the modifications found so far to equation (4) leads to a ratio of $\sim 7 \times 10^{-8}$, which is within a factor of 2 of the observed ratio. Thus, the chemistry of CH in clouds detected by optical absorption lines is adequately described by incorporating the modifications necessary for the C_2 chemistry and by decreasing the rate for radiative association between C^+ and H_2.

b) CO *Chemistry*

The production of CO is dominated by reactions between C^+ and OH, with a 20% contribution from reactions involving atomic oxygen and the carbon-bearing molecules CH and C_2 for clouds with $A_V \sim 4$ mag. This small contribution from CH and C_2 applies when the C^+ abundance is one-fifteenth the value at 1 mag of extinction; *thus, neutral reactions of carbon-bearing molecules always play a minor role in the formation of CO.* The carbon ion also reacts with $\mathrm{H}_2\mathrm{O}$ (Anicich and Huntress 1986), but ultraviolet measurements of clouds with 1 mag of extinction have yielded upper limits to $N(\mathrm{H}_2\mathrm{O})$ that are at least 10 times smaller than the observed values for $N(\mathrm{OH})$ (Smith and Snow 1979). The results of Smith and Snow lead to the conclusion that in light of the recently evaluated photodissociation rate for OH (van Dishoeck and Dalgarno 1984), which is relatively large, the dissociative electron recombination of $\mathrm{H}_3\mathrm{O}^+$ favors OH over $\mathrm{H}_2\mathrm{O}$ (see Herbst 1978). Therefore, the only oxygen-bearing species considered in our analysis of the CO chemistry is OH. Possible consequences of including production through reactions with $\mathrm{H}_2\mathrm{O}$ are discussed in the next section.

The rate equation for CO is

$$N(\mathrm{CO}) = \frac{k_6\, n(\mathrm{C}^+) N(\mathrm{OH}) + n(\mathrm{O})[k_4\, N(\mathrm{CH}) + k' N(\mathrm{C}_2)]}{G(\mathrm{CO}) + k_7\, n(\mathrm{He}^+)}\ \mathrm{cm}^{-2} . \tag{7}$$

The reactions $\mathrm{C}^+ + \mathrm{OH} \rightarrow \mathrm{CO}^+ + \mathrm{H}$ and $\mathrm{He}^+ + \mathrm{CO} \rightarrow \mathrm{He} + \mathrm{C}^+ + \mathrm{O}$ have rate coefficients k_6 and k_7. All the reactions and the values for their rate coefficients appear in Table 1. The photodissociation rate $G(\mathrm{CO})$ has to include the effects of self-shielding (e.g., Glassgold, Huggins, and Langer 1985). The helium ion arises from cosmic-ray ionization.

When the observations for a cloud with A_V of 1 mag are analyzed, where photochemistry plays a major role, the expression for $N(\mathrm{CO})$ becomes

$$N(\mathrm{CO}) \rightarrow \frac{k_6\, n(\mathrm{C}^+) N(\mathrm{OH})}{G(\mathrm{CO})}\ \mathrm{cm}^{-2} . \tag{8}$$

Equation (8) yields a value of 8.7×10^{15} cm^{-2} for $N(\mathrm{CO})$ using an estimate for the Langevin rate coefficient of 2.9×10^{-9} cm^3 s^{-1} for k_6, an abundance of 2.5×10^{-4} for C^+, and a rate of 10^{-12} s^{-1} for $G(\mathrm{CO})$. A column density of 3×10^{13} cm^{-2} for OH, appropriate for the direction to ζ Oph (Crutcher and Watson 1976), is incorporated into the rate equation. The Langevin rate coefficient is again based on the ADO theory of Su and Chesnavich (1982). The value for $G(\mathrm{CO})$ is an estimate based on the results of Glassgold, Huggins, and Langer (1985) and van Dishoeck and Black (1988). The derived value for $N(\mathrm{CO})$ compares favorably with the observed value of 2.3×10^{15} cm^{-2} for the cloud toward ζ Oph (Morton 1975). The calculated value for $N(\mathrm{CO})$ can be decreased by increasing the photodissociation rate several fold, as has been suggested by van Dishoeck and Black (1986) in their chemical study of the ζ Oph cloud.

For a more opaque cloud ($A_V \sim 4$ mag), the rate equation (7) for $N(\mathrm{CO})$ includes only $k_7\, n(\mathrm{He}^+)$ as a destruction term, with a value for the rate coefficient of 1.6×10^{-9} cm^3 s^{-1} (Anicich and Huntress 1986). For $N(\mathrm{CH})$ and $N(\mathrm{C}_2)$, the results for the gas toward HD 29647 are representative, while an estimate for $N(\mathrm{OH})$ is obtained from the correspondence between $N(\mathrm{OH})$ and A_V (Crutcher 1979): A column density of 8×10^{13} cm^{-2} for OH represents 1 mag of extinction. Since the density for He^+ is not known *a priori*, the rate equation for CO can be inverted to deduce the required value for $n(\mathrm{He}^+)$. In particular, for the cloud toward HD 29647, Crutcher (1985) measured the CO emission and found that $N(\mathrm{CO}) \sim 3 \times 10^{17}$ cm^{-2}. This value for $N(\mathrm{CO})$ is reproduced to within a factor of 2 when $n(\mathrm{He}^+)$ is in the range 1.5×10^{-5} to 6×10^{-5}.

To test whether or not this range for $n(\mathrm{He}^+)$ is acceptable, we look at the rate equation for He^+:

$$n(\mathrm{He}^+) = \frac{\zeta_{\mathrm{He}}\, x(\mathrm{He})}{k_9\, x(\mathrm{H}_2) + k_7\, x(\mathrm{CO})}\ \mathrm{cm}^{-3} . \tag{9}$$

Here, ζ_{He} is the cosmic-ray ionization rate for He; k_9 (1.0×10^{-13} cm^3 s^{-1}; Anicich and Huntress 1986) is the coefficient for the reaction between He^+ and H_2. A test of the reasonableness of the derived range in $n(\mathrm{He}^+)$ would be to obtain the corresponding range in ζ_{He} from equation (9) with values for $x(\mathrm{He})$, $x(\mathrm{H}_2)$, and $x(\mathrm{CO})$ of 0.1, 0.5, and 10^{-4}, respectively. The corresponding range in ζ_{He} is 3×10^{-17} s^{-1} to 1.2×10^{-16} s^{-1}, which is equivalent to a range for the primary cosmic-ray ionization rate of 2–8 × 10^{-17} s^{-1} (see Glassgold and Langer 1974).

Chemical models for a cloud with $A_V \sim 1$ mag by van Dishoeck and Black (1986) indicate primary cosmic-ray ionization rates of 4–20 × 10^{-17} s^{-1}. Their values set an upper limit to the rate because they assumed all the OH forms via an ion-molecule scheme; some of the OH may form under other applicable schemes, such as shock chemistry. Even with this caveat, our analysis for a cloud with $A_V \sim 4$ mag yields a slightly smaller rate and may reveal the presence of the screening of cosmic rays from the interiors of clouds by magnetic fields (Hartquist, Doyle, and Dalgarno 1978). If there were no decrease in the abundance of C^+, a primary rate larger than the rate for a less opaque portion of a cloud would be required to bring the theoretical prediction into agreement with observations! Thus *the simplest picture for the chemistry of CO incorporates the decrease in* $x(C^+)$, *as required by the* C_2 *and* CH *chemistries, and a primary ionization rate somewhat lower than the value deduced for regions with* 1 mag *of extinction.*

IV. DISCUSSION

The analytical approach introduced by Federman, Danks, and Lambert (1984) and Federman and Lambert (1988) as a guide to the study of CN chemistry has been extended to the chemistries of C_2, CH, and CO. When column densities for the progenitor molecules are used in the rate equations, the chemistry for a specific molecule is isolated from the larger chemical network. The approach, which delineates the basic chemistry, is shown to be very useful in that modifications to one of the rate equations applies equally well to the other rate equations. These modifications include a decrease in the abundance of C^+ for the most reddened clouds studied, reductions in rate coefficients for reactions that initiate the chemistry, and an estimate for the cosmic ray ionization rate in a cloud with 4 mag of extinction.

The suggested decrease in the abundance of C^+ for the more opaque clouds implies that $x(C^+) \sim x(\text{C I})$ (J. Keene, private communication). For these clouds $N(\text{CO}) \sim 3 \times 10^{17}$ cm^{-2} (Crutcher 1985). The use of the relation between $E(B-V)$ and $N(H_2)$ from Bohlin, Savage, and Drake (1978) yields a column density for H_2 of $\sim 4 \times 10^{21}$ cm^{-2}. Thus most of the gas-phase carbon is in the form of CO because $x(\text{CO}) \sim 10^{-4}$; an enhancement in the depletion of carbon by a factor of 2–3 over the depletion in the clouds toward stars in Perseus and Ophiuchus probably accounts for the remainder of the carbon. This comparison shows that most of the decrease in $x(C^+)$ arises from the conversion of C^+ into CO. For these moderately reddened clouds, $x(C^+) \sim x(\text{C I}) \sim 0.1x(\text{CO})$.

Several previous studies also discussed a decrease in $x(C^+)$ as a function of depth into a cloud. For instance, the theoretical calculations of Langer (1976), de Jong, Dalgarno, and Boland (1980), and Boland and de Jong (1984) predicted the decrease; here we have shown that the analysis of recent observations substantiates the theoretical prediction. Moreover, these data indicate that the decrease is approximately linear from 1 mag to 4 mag. The analysis of Federman and Lambert (1988) in terms of two simple, constant density and temperature calculations with rate equations similar to ours leads to the requirement of a decrease in the ionized carbon abundance. We have quantified this conclusion of Federman and Lambert by examining the chemistry for individual directions and by discerning that the decrease is linear—see Figure 1.

Our analysis requires a rate coefficient of $\sim 3 \times 10^{-10}$ cm^3 s^{-1} for the ion-molecule reaction that initiates the production of C_2. If a value for the total rate coefficient for $C^+ + \text{CH}$ differed from 2.7 × 10^{-9} cm^3 s^{-1}, then the branching ratios for the various channels would have to be revised accordingly. Since we have lessened the importance of the reaction between C^+ and CH, another possible route to C_2, starting with $C^+ + CH_2$, has to be considered. However, the observed amount of CH is used in our analysis, and our predictions are larger than the observations for $N(C_2)$. Thus, if production of C_2 occurred through reactions involving both CH and CH_2, then the rate coefficient for reaction (3a) would have to be *decreased further.* A detection of CH_2 is necessary to quantify the effects of CH_2 on the chemistry of C_2; theoretical calculations yield $N(CH_2) \sim 10^{13}$ cm^{-2} for the cloud toward ζOph (van Dishoeck and Black 1986; Viala, Roueff, and Abgrall 1988). The upper limit measured by Snow (1976), which depends on an unknown oscillator strength, may be in conflict with these predictions.

The calculations of Nercessian, Benayoun, and Viala (1988) for the line of sight to HD 29647 appeared in print during the writing of the present paper. They were able to reproduce the available data for this cloud of 4 mag of extinction with a constant density model. This fact adds weight to our premise that many aspects of the chemistry can be studied through a simple model of a cloud. Nercessian, Benayoun, and Viala also found that carbon is depleted by an extra factor of 2 and that C^+ is converted into CO in the cloud toward HD 29647. The linear decrease in $x(C^+)$ found by us suggests that sulfur is not as depleted as in the "best" model of Nercessian *et al.* They require a similar cosmic-ray ionization rate (5 × 10^{-17} s^{-1}) in order to model the chemistries of HCO^+ and OH.

Bates (1986) has suggested that dissociative electron recombination favors the removal of a single hydrogen atom, while Herbst (1978) has found theoretically that in some systems the removal of two hydrogen atoms is preferred. This difference affects the chemistries of C_2 and CO. In the case of C_2 chemistry, the branching ratio for the reaction $C_2H_2{}^+ + e^-$ has been chosen to favor C_2 over C_2H. The consequences of favoring C_2H production now are addressed. If the rate coefficient for $C_2H + O$ is small because of the presence of an activation energy (see Prasad and Huntress 1980), no change in our conclusions would arise. If, however, the reaction between C_2H and O proceeds, a factor of 0.5–1.0 would appear in the numerator of equation (2), thus requiring a smaller reduction in k_3. However, a factor of 2 uncertainty in the analysis is anticipated in any case.

A more meaningful test of the two theoretical formulations for electron recombination can be obtained from the CO chemistry because of the dependence of CO formation on the products from the recombination of H_3O^+. For the cloud toward ζ Oph, $N(\text{OH}) \gg N(H_2O)$ (Snow and Smith 1981). Only a small fraction of the difference in column densities is attributable to the large photodestruction rate for water because OH also has a large rate (van Dishoeck and Dalgarno 1984). In the cloud toward HD 29647, where $A_V \sim 4$ mag, reactions between C^+ and H_2O would increase the analytically derived values for $N(\text{CO})$ substantially above the observed value. Our analyses indicate that the theory of Herbst (1978) is more appropriate to the H_3O^+ system.

More observational data on OH could test this conclusion because the slope of $N(\text{OH})$ versus $N(H_2)$ reveals where in the chemical chain OH forms (cf. Federman, Danks, and Lambert 1984). A slope of unity would indicate that OH formation is the primary route for H_3O^+ recombination, while a slope of two would indicate that OH formation occurs through the dissociation of H_2O. The necessary absorption measurements are possible with the high-resolution spectrometer on the Hubble Space Telescope. Even when the recombination favors OH, a substantial amount of H_2O is formed under conditions appropriate to a cloud interior (Sternberg, Dalgarno, and Lepp 1987). The amount for H_2O predicted by Sternberg *et al.* would lead to a column density for N(CO) in conflict with observations; a way around this dilemma is to invoke water condensation onto grains.

A clearer understanding of the basic chemistry in diffuse interstellar clouds is emerging. The analytical approach for CN, C_2, CH, and CO used in this paper reveals key aspects of the chemistry. Detailed analysis of the excitation and chemistry for specific clouds (e.g., van Dishoeck and Black 1986) reveals the physical conditions, such as temperature, density, and ambient radiation field. Log-log plots of the observed column density for a molecule against $N(H_2)$ reveal from the slope whether the observations apply to photochemical or chemical collision regimes. In the photochemical regime, these plots also indicate the stage in the network where the molecule forms (Federman, Danks, and Lambert 1984; Federman and Lambert 1988). Thus a stronger foundation for chemical models of dark clouds is now available.

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