

Chemical Processes in the Shocked Interstellar Gas [and Discussion]

A. Dalgarno and D. R. Flower

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Chemical processes in the shocked interstellar gas

BY A. DALGARNO, F.R.S.

*Harvard–Smithsonian Center for Astrophysics, 60 Garden Street,
Cambridge, Massachusetts 02138, U.S.A.*

A review is presented of molecular formation and destruction processes in shocked interstellar gas, and the chemistry of some particular regions of the interstellar medium is briefly discussed.

1. INTRODUCTION

Shock waves occur in compressible media when the pressure gradients are large enough to generate supersonic motion. Because the shock propagates faster than the velocity of sound, the medium ahead of the shock cannot respond dynamically to the shock until it arrives. The shock then compresses, heats and accelerates the medium. A fast shock will excite, dissociate and ionize the gas. The subsequent recombination and emission produces X-ray and ultraviolet photons, which ionize and dissociate the gas ahead and behind the shock. This precursor radiation modifies substantially the thermal and dynamical evolution of the shocked material. The presence of a magnetic field can change the nature of a shock. Indeed, if the fractional ionization is low, a shock may be preceded by a magnetic precursor, which heats and compresses the material ahead of the shock front (Draine 1980).

Shocks are a ubiquitous phenomenon in interstellar space, occurring during the birth and the death of stars. Ultraviolet photons emitted by a star ionize the gas around it, raise the pressure and drive a shock into the medium. Stronger shocks are produced by stellar winds from early type stars, by collisions of interstellar clouds and by supernova explosions. On a larger scale, shock waves initiate bursts of star formation as the increase in pressure triggers the gravitational collapse and fragmentation of dense clouds.

The history of a dense shocked gas is sensitive to the molecular composition. The molecular abundances depend in detail on the physical conditions in which the shock develops, and molecular observations constitute a unique diagnostic probe of the shock environment. Of particular utility are infrared observations of emissions from excited rotation–vibration levels, which provide a direct measure of the cooling of the heated post-shock gas.

A diverse array of physical and chemical processes occurs in shocked gases. A review of many of them has been presented by McKee & Hollenbach (1980), who also summarize the observational evidence for shock waves in the interstellar gas.

Molecular dissociation processes are crucial to the analysis and interpretation of shocks propagating in clouds with densities exceeding about 10^2 cm^{-3} . Molecular dissociation may occur by collisions of molecules with neutral particles and electrons, by photodissociation and by chemical reactions.

2. DISSOCIATION PROCESSES

2.1. *Collision-induced dissociation*

Collision-induced dissociation is the process



by which a molecule XY is dissociated by collisions with an atomic or molecular species M. In the interstellar medium, M is either H or H₂. The process has been studied extensively in the laboratory for several molecules and values of the effective dissociation rate coefficient κ_d have been inferred. A list of the experimental values has been compiled by Hollenbach & McKee (1979).

The laboratory measurements were carried out at high densities, where collisions are frequent and radiative processes can be neglected. In gases of high density, collision-induced dissociation is a complex process involving multiple transitions between the rotation–vibration levels of the molecule in which a quasi-equilibrium distribution of the level populations is obtained. Dissociation occurs preferentially by neutral particle impact excitations into the vibrational continuum from the high-lying rotation–vibration levels that have been populated by sequential excitations of the lower levels. The formal theory of collision-induced dissociation is well developed (see Yau & Pritchard 1979) but there remain considerable uncertainties in the efficiencies of the individual energy transfer processes between the discrete levels and to the dissociation continuum.

At lower densities radiative processes must be incorporated. There occurs a competition with the collision processes, and the effective collision-induced dissociation rate coefficient depends upon the density $n(M)$ of the collision partner M. In optically thin cases, the radiative processes diminish the populations of the excited levels and radiative stabilization can drastically reduce the efficiency of collision-induced dissociation. Large differences occur between homonuclear molecules for which radiative stabilization is slow and heteronuclear molecules for which it is rapid. Dalgarno & Roberge (1979) extended the standard master equation description of collision-induced dissociation to include the effect of spontaneous radiative decays, and they presented preliminary estimates of κ_d for the processes



and



for a range of gas densities and temperatures. In a more recent analysis, revised estimates of κ_d for (2) were obtained and the method was extended to the reaction



(Roberge & Dalgarno 1981). The calculations do not take into account transitions involving changes in vibrational quantum numbers exceeding unity and they omit the excitations from low-lying vibrational levels directly into the continuum, which determine the rate coefficient in the limit of low densities. Quasi-classical trajectory calculations (Blais & Truhlar 1981) suggest that a value of $10^{-17} \text{ cm}^3 \text{ s}^{-1}$ is a probable lower limit to κ_d at 4500 K, but a more extensive set of collision cross section data is needed for a precise calculation of κ_d at low densities.

At high densities, the theoretical values of κ_d for (2) and (4) were constrained to match the laboratory data of Breshears & Bird (1973). The calculations suggest that for temperatures below

10 kK, the laboratory values of κ_d for (2) are valid only for densities $n(\text{H}) > 10^5\text{--}10^6 \text{ cm}^{-3}$ and for (4) only for $n(\text{H}_2) > 10^6\text{--}10^7 \text{ cm}^{-3}$. At densities below 10^5 cm^{-3} the rate coefficients decrease rapidly with decreasing density, and collision-induced dissociation becomes inefficient.

The effect of radiative stabilization is greatly enhanced for heteronuclear molecules (Dalgarno & Roberge 1979). Recent calculations by Roberge & Dalgarno (1981) for (3) show that at a temperature of 20 kK, densities exceeding 10^{10} cm^{-3} must be obtained to reach the high density limit. At lower densities κ_d quickly becomes small as it tends to values determined by the direct excitation of low-lying levels into the vibrational continuum. In astrophysical shocks other dissociation processes are usually more efficient and it appears that with the possible exception of HD, collision-induced dissociation of heteronuclear molecules may be neglected.

The radiative lifetimes of the vibrational levels of heavy homonuclear molecules such as O_2 are longer than for H_2 , and the effects of radiative stabilization on the collision-induced dissociation of O_2 are smaller. Nevertheless other dissociation mechanisms will usually prevail.

2.2 Electron impact dissociation

In electrical discharges, molecular dissociation occurs primarily by electron impact excitations. In H_2 dissociation proceeds through a transition from the ground $X^1\Sigma_g^+$ electronic state to the excited repulsive $b^3\Sigma_u^+$ state,



(see Capitelli *et al.* 1977). Fast shocks ionize the gas and at low densities the rate of dissociation is controlled by the excitation process (5). The cross sections of (5) have been measured by Corrigan (1965) and the thermal rate coefficient has been calculated by Capitelli *et al.* (1977). The cross section measured by Corrigan (1965) has a threshold at 8.8 eV which is lower than that found in theoretical calculations (Fliflet & McKoy 1980; Weathergood 1980). The difference is not insignificant in considerations of the minimum shock velocity that leads to dissociation of H_2 in a low-density gas.

At higher densities, dissociation is complicated by transitions between vibration-rotation levels, by excitations to discrete electronic levels followed by radiative decay into the vibrational continuum and into excited vibrational levels of the ground electronic state, and by contributions from dissociative attachment,



Hollenbach & McKee (1980) have explored the contributions of process (5) to dissociation in a shocked gas and conclude that at low densities less than about 10^2 cm^{-3} the process leads to complete destruction of molecular hydrogen for shocks propagating with velocities in excess of 50 km s^{-1} . As radiative effects diminish in importance, the critical dissociation velocity decreases with increasing density to a value of 25 km s^{-1} for densities greater than about 10^4 cm^{-3} (Kwan 1977; Hollenbach & McKee 1980).

Other molecules are destroyed by collisions with energetic electrons, and no molecule survives a fast shock even in a low density gas. Those with lower thresholds than H_2 may be dissociated by electron impacts in régimes in which hydrogen remains molecular, but because H_2 is the major constituent a small fractional dissociation provides an abundance of hydrogen atoms that may participate in chemical reactions with the different molecular species and lead to their destruction.

2.3. Chemical reactions

At the elevated temperatures of shock-heated gas, the chemistry is quite unlike that of cold interstellar clouds, which is dominated by ion–molecule reactions (see Klemperer, this symposium). In hot gas, activation barriers in exothermic reactions can be surmounted, endothermic reactions may proceed rapidly and the chemistry is controlled by simple exchange reactions involving the major constituents H and H₂ (Aannestad 1973; Iglesias & Silk 1978). Effective dissociation of a molecule XY occurs through the sequences



and



and the dissociation of XY is linked to the dissociation of H₂. Only those molecules with large dissociation energies, such as CO, can long persist after the dissociation of H₂ is initiated. Hollenbach & McKee (1980) have carried out detailed calculations of the limiting shock velocities, above which dissociation is achieved in a fully molecular gas, which demonstrates the importance of the chemical reactions (7) and (8). Except for CO in a high-density gas, the limiting velocities for the various molecules are smaller than those for H₂. For O₂ in a high-density gas, the velocity is 11 km s⁻¹ compared with 25 km s⁻¹ for H₂. The small abundance of oxygen limits the effectiveness of the chemical sequence initiated by



as a destruction mechanism for H₂.

Hollenbach & McKee (1980) also explored the influence of the ion–atom interchange process



but at temperatures where the process might contribute, it proceeds less rapidly than dissociation by electron impact.

2.4. Photodissociation

Fast shocks produce X-rays and ultraviolet photons, which dissociate the molecules existing in the pre-shock gas and which retard the formation of molecules in the post-shock gas. For shocks with velocities between 50 and 200 km s⁻¹ the photon fluxes have been calculated by Raymond (1979) and Shull & McKee (1979). The short wavelength radiation is absorbed in transition zones around the ionized regions of the gas and degraded to wavelengths longer than 91.2 nm. Little of the radiation appears as ultraviolet continuum and a detailed description of the line emissions is required together with high-resolution photodissociation cross section data to predict the dissociation lifetimes. The destruction of molecular hydrogen by the absorption of continuum radiation in the Lyman and Werner band systems followed by spontaneous radiative dissociation, which is the main loss mechanism for H₂ in diffuse interstellar clouds, is not efficient in shocked gases (Hollenbach & McKee 1979) unless there is a nearby external source of ultraviolet photons.

Because of radiation trapping by hydrogen atoms, a large fraction of the ultraviolet energy emitted by the shocked gas appears in the form of Ly α photons. Fluorescence of Ly α by vibrationally excited H₂ has been identified in sunspots (Jordan *et al.* 1977) and T Tauri (Brown *et al.* 1981) and may occur in supernova remnants (Benvenuti *et al.* 1980). The possible fluorescence of Ly β, which is absorbed by the $J = 1, v = 0$ level of H₂ in supernova remnants, has been

pointed out by Raymond *et al.* (1981). There may be other near coincidences with strong lines. Some of these line absorptions lead to dissociation of H_2 .

Absorption by vibrationally excited molecules may affect the photodissociation of O_2 . Molecular oxygen in its ground vibrational state is a weak absorber of Ly α but the photodissociation cross section probably increases rapidly with vibrational quantum number.

Heteronuclear molecules are mostly in their lowest states and vibrational effects on photodissociation can be ignored. Because of the importance of Ly α there are interesting differences between molecules. The molecule CO is not photodissociated by Ly α but most other interstellar species, and in particular OH, H_2O and CH_4 , absorb Ly α strongly. Ly α also photoionizes some interstellar molecules such as NO and HCO.

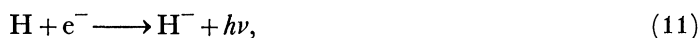
3. FORMATION PROCESSES

3.1. Grain catalysis

The survival of grains in a shock has been discussed recently by Draine & Salpeter (1979), and the formation of molecules on shocked grain surfaces by Hollenbach & McKee (1980). It appears that H_2 can be formed on grain surfaces in the cooling post-shock gas, though probably at a slower rate following shocks with velocities greater than about 100 km s^{-1} because of the destruction of the grain mantles.

3.2. Chemical reactions

Even in the absence of grains, H_2 can be formed in a hot ionized gas by the sequences



and



The formation of H_2 is followed by reactions of the kind



(Aannestad 1973), which may be endothermic. Because heteronuclear molecules are mostly in the lowest rotation-vibration level in astrophysical shocks, chemical rate coefficients measured at high temperatures in the laboratory may not be directly applicable (see Herbst & Knudson 1981). In a model of an OH maser produced behind a 10 km s^{-1} shock, Elitzur & de Jong (1978) invoked the reactions



and



and Elitzur (1979) proposed the same sequence as the source of the high H_2O abundance detected in Orion (Phillips *et al.* 1978; Waters *et al.* 1980). Elitzur & Watson (1978, 1980) have suggested that the observed interstellar CH^+ molecules are produced in shocks associated with expanding H II regions by the reaction



Heavy molecules are formed by reactions of hydrides



or



Then CO is a product of the reactions



and



Iglesias & Silk (1978) studied the consequences of reactions (15), (19) and (20) behind a 10 km s^{-1} shock propagating in a dense molecular cloud and concluded that CO, NH_3 , HCN and N_2 are unaffected by the shock, that H_2CO , CN and HCO^+ are reduced in abundance and that large quantities of H_2O , HCO and CH_4 are produced. Hartquist *et al.* (1980) carried out a similar study of the chemistry of sulphur-bearing molecules and pointed out that they may be specific indicators of heated gas. In cold gas, none of the suggested mechanisms for the formation of molecules containing sulphur (Oppenheimer & Dalgarno 1974; Duley *et al.* 1980) is rapid, and the chemical schemes predict low abundances. In a heated gas, the sulphur chemistry is initiated by the endothermic reactions



or



and substantial enhancements of SO, CS, OCS and H_2S are expected.

No calculation has yet been presented of the molecular composition after a dissociative shock, though Hollenbach & McKee (1979) have summarized the physical and chemical processes. The composition will depend on the physical environment of the shock and the cooling processes occurring in the post-shock gas. If the oxygen is rapidly taken up in H_2O , the carbon will tend to reside in CH_4 and the composition will be entirely different from that expected from a non-dissociative shock.

4. CHEMICAL EVIDENCE FOR SHOCKED GAS

I shall consider briefly the molecular composition in three regions where shocks may be propagating.

4.1. *The Kleinman–Low nebula*

Several molecular species have been detected in the vicinity of the Kleinman–Low nebula in Orion with unusually broad emission lines. The high velocity emissions appear as a pedestal of width of about 35 km s^{-1} upon which a brighter narrow spike of width 4 km s^{-1} is superimposed. The high velocities suggest that a shock must be formed (Kwan & Scoville 1976), and what appears to be confirming evidence is provided by infrared observations near $2 \mu\text{m}$ of emission from vibrationally excited molecular hydrogen (see Beckwith 1980) consistent with a thermal excitation temperature of 2000 K.

Zuckerman & Palmer (1975) pointed out that the chemical abundances in the pedestal source are quite different from those in the large Orion molecular cloud. The high-velocity gas shows up strongly in H_2S , SO, SO_2 and SiO (Thaddeus *et al.* 1972; Gottlieb & Ball 1973; Snyder *et al.* 1975; Dickinson *et al.* 1976; Lada *et al.* 1978; Genzel *et al.* 1980; Welch *et al.* 1981). The enhanced abundances of sulphur-bearing species and of SiO are qualitatively consistent with the molecular composition of a hot gas (Hartquist *et al.* 1980). The shock model of Hartquist *et al.* (1980) also

predicts an enhancement in the abundance of CS, though smaller than for the other sulphur molecules. No enhancement is observed for CS (Goldsmith *et al.* 1980). Because of the destruction reaction



the CS abundance is sensitive to the distribution of oxygen in the cooling post-shock gas. Goldsmith *et al.* (1980) suggest plausibly that the fraction of oxygen in atomic form has been underestimated.

The shock models predict enhancements in H₂O and OH. An enhanced OH/H₂ ratio has been inferred by Storey *et al.* (1981) from observations of two lines of OH in emission at 119.23 and 119.44 μm from near the Kleinman–Low nebula. The emission lines originate in the ²Π_{3/2}, J = 5/2 level of OH and their presence indicates a temperature of at least 500 K. A similar temperature is required to produce the emission lines from high rotational levels of CO detected by Watson *et al.* (1980).

The large H₂O abundances (Phillips *et al.* 1978; Waters *et al.* 1980) are also suggestive of a heated shocked gas chemistry (Elitzur 1979). However, H₂O was not detected in several other locations where shock waves seem likely (Waters *et al.* 1980).

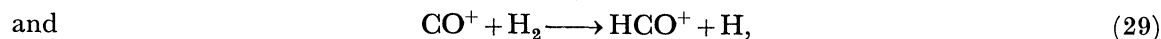
The deuterated molecule HDO has been detected in the direction of the Kleinman–Low nebula (Turner *et al.* 1975). The derived HDO/H₂O abundance ratio lies between 2 × 10⁻³ and 2 × 10⁻² (Waters *et al.* 1980), indicating substantial fractionation. Such a large fractionation is difficult to achieve in a heated gas.

4.2. IC 443

IC 443 is a supernova remnant in which vibrationally excited H₂ has been observed at a velocity of 30 km s⁻¹ (Treffers 1979), together with several radio molecules (DeNoyer 1979; Dickinson *et al.* 1980; DeNoyer & Frerking 1981). Shock wave acceleration is a plausible explanation of the rapidly moving gas. DeNoyer & Frerking (1981) observed a 100-fold increase in the OH/CO abundance ratio, but in contrast to the Orion pedestal source found no enhancement in any of HCN, CS, SO or SiO. The shock enhancement in the sulphur molecules is sensitive to the H/H₂ ratio but the lack of enhancement of SiO is unexpected. DeNoyer & Frerking (1981) suggest that either



is a slow reaction or silicon is severely depleted. The shock calculations of Iglesias & Silk (1978) show no enhancement in HCN, in harmony with observation, but they predict a decrease in the HCO⁺/CO abundance ratio, whereas Dickinson *et al.* (1980) and DeNoyer & Frerking (1981) observed an increase of at least an order of magnitude. The enhancement of H₂O and OH will increase the source of HCO⁺ through the reactions



but the C⁺ ions are preferentially removed by a sequence initiated by (18). Associative ionization reactions such as



which become rapid at higher temperatures may be important. In the model of Iglesias & Silk (1978), HCO is produced in abundance and additional sources of HCO⁺ are charge transfer of

positive ions with HCO and photoionization. The chemistry may also be modified by radiation produced in the supernova remnant. Detailed calculations are needed.

4.3. *Ophiuchi*

Crutcher (1979) has found evidence that the OH seen towards ζ Ophiuchi has two components, separated in velocity by about 5.5 km s^{-1} , and he locates one component in the pre-shock gas and the second in the post-shock gas. Frisch (1979) and Federman (1980) have advanced similar interpretations of observations of CN and CH^+ made towards χ Ophiuchi and ζ , θ and ξ Persei. The observations are qualitatively consistent with a shock model proposed by Elitzur & Watson (1978, 1980) to explain the interstellar abundances of CH^+ through reaction (18). The model is not without quantitative difficulty. To reproduce the measured abundances of CH^+ requires special assumptions about the pre-shock H/H_2 ratio and gas density, and the model tends to predict excessive amounts of OH and H_2O , particularly when the effect of radiative stabilization in limiting the dissociation of H_2 is taken into account. Some of the difficulties may be resolved by including the contribution of emissions from OH to the cooling of the shocked gas (Flower & Hartquist 1981), by a more accurate treatment of photodissociation processes and by taking account of the effects of the interstellar magnetic field. Ambipolar diffusion imparts a drift velocity to the positive ions (see Black & Hartquist 1979), which may enhance the relative effectiveness of (15) compared with the neutral particle reactions (16) and (17). The detection of other molecular ions such as SiH^+ , SH^+ and HCl^+ is potentially an independent measure of the appropriateness of the shock model.

Molecular observations in the radio and infrared regions of the spectrum provide valuable information on the physical conditions and the sources of energy of a diverse range of astronomical phenomena where shock waves occur. More detailed models of the velocity, density and temperature distributions of shocked regions are needed to work out the chemical consequences and to interpret the observational data.

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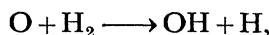
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Discussion

D. R. FLOWER (*Department of Physics, Durham University, U.K.*). I wish to elaborate on some remarks of Professor Dalgarno by briefly describing recent work by T. W. Hartquist and myself.

In the shocked molecular regions of interstellar space, the abundance of the OH radical is expected to be relatively high (Elitzur & de Jong 1978). The high temperature behind the shock favours the (endothermic) reaction



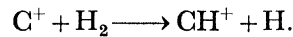
resulting in $10^{-5} \text{ cm}^{-3} \lesssim n(\text{OH})/n(\text{H}_2) \lesssim 10^{-4} \text{ cm}^{-3}$.

The rate of cooling of these regions by rotational-vibrational transitions of H_2 has been computed by Hartquist *et al.* (1980). As the spectrum of H_2 is quadrupolar, the radiative transition probabilities are small, and a thermal distribution of level populations is attained for

$$n(\text{H}_2) \gtrsim 10^6 \text{ cm}^{-3}.$$

It follows that at higher densities the rate of cooling per unit volume by H_2 is proportional to $n(\text{H}_2)$. However, the OH radical has a dipole spectrum, and collisional excitation of rotational transitions in OH is followed by radiative decay. Consequently, the rate of cooling per unit volume by OH continues to rise in proportion to $n^2(\text{H}_2)$ beyond $n(\text{H}_2) = 10^6 \text{ cm}^{-3}$. By using the values of the cross sections for the rotational excitation of OH by H_2 computed by Dewangan & Flower (*J. Phys. B* **14**, 2179 (1981)), it may be shown that OH cooling dominates H_2 cooling in shocked regions where $n(\text{H}_2) \gtrsim 2 \times 10^6 \text{ cm}^{-3}$. Such densities are believed to be readily attained behind shocks and we conclude that it is essential to include OH cooling in quantitative models. Indeed, in regions of OH maser emission, such as W3 OH, we estimate that the flux reaching the Earth in the far infrared rotational transitions of OH ($50 \mu\text{m} \lesssim \lambda \lesssim 170 \mu\text{m}$) should be sufficient ($10^{-16} \text{ W cm}^{-2}$) to be detectable with current receivers.

A further reaction, believed to be important in shocks, is



Elitzur & Watson (1978, 1980) have proposed that the longstanding discrepancy between the predicted and observed column densities of CH^+ may be resolved by appeal to CH^+ formation through this (endothermic) process. However, consideration of the relevant timescales shows that OH cooling may be expected to be at least as important as cooling by H_2 in these regions, and the rate of formation and column density of CH^+ may have been overestimated. Detailed calculations are necessary to confirm this hypothesis.