

The gas-phase destruction of interstellar carbon dioxide: Calculations on the reactions between CO₂ and H₂ and between CO₂ and H

D. Talbi¹ and E. Herbst²

¹ LETMEX, Université de Nice Sophia Antipolis, Parc Valrose, U.F.R. Sciences, 06108 Nice Cedex 2, France

² Departments of Physics and Astronomy, The Ohio State University, Columbus, OH 43210, USA

Received 27 December 2001 / Accepted 28 February 2002

Abstract. Carbon dioxide is an abundant component of cold interstellar grains, but its gas-phase abundance is not high. To partially explain this low abundance, it has been suggested that gas-phase CO₂ is destroyed by reaction with both atomic and molecular hydrogen. Although there are experimental studies concerning the rate of the reaction between CO₂ and H, there are no modern experimental studies for the analogous reaction with H₂. In this paper, we report quantum chemical and dynamical research on the reactive systems CO₂ + H and CO₂ + H₂. Our results for the former are in excellent agreement with experiment and previous theory, while our results for the latter show this reaction to possess an extremely large potential energy barrier, far in excess of the reaction endothermicity.

Key words. ISM: abundances – ISM: molecules – molecular processes

1. Introduction

Carbon dioxide is a major component of dust mantles in giant molecular clouds (Gerakines et al. 1999; Whittet et al. 1998; de Graauw et al. 1996). In hot core sources, where dust mantles appear to be evaporated during warming and to be sputtered in shock waves, one might expect to observe large abundances of gaseous CO₂, but this is not the case (van Dishoeck et al. 1996; van Dishoeck 1998; Boonman et al. 2000; Charnley & Kaufman 2000; Doty et al. 2002). Two possible reactions which can destroy gaseous carbon dioxide efficiently are



and



The first reaction has been studied in the laboratory over a wide range between room temperature and more than 10 000 K; its rate coefficient k_1 has been measured to be $2.5 \times 10^{-10} \exp(-13\,300/T) \text{ cm}^3 \text{ s}^{-1}$ in the range 300–2500 K, and $3.3 \times 10^{-10} \exp(-13\,500/T) \text{ cm}^3 \text{ s}^{-1}$ in the range 2170–3150 K (Tsang & Hampson 1986; Lissianski et al. 1995). The reaction is endothermic by 12 300 K (Lias et al. 1988) so that the barrier to reaction is not significantly in excess of the endothermicity. Although this reaction has been studied theoretically

(Schatz et al. 1987), the reverse (exothermic) reaction is possibly of more theoretical interest because of the possibility that it occurs at low temperatures and leads to the formation of gas-phase CO₂ (Smith 1988).

Reaction (2) has not been studied in the laboratory. Endothermic by only 4860 K (Lias et al. 1988), the reaction appears to have a large activation energy barrier. A rather old experimental study by Graven & Long (1954) at 1173 K suggests that even at this elevated temperature, the rate of the reaction is far slower than an alternative pathway to the production of CO and H₂O: dissociation of molecular hydrogen followed by reaction (1) and the reaction



The UMIST rate file (Le Teuff et al. 2000) lists a relatively large rate coefficient k_2 of $2.94 \times 10^{-14} \exp(-7550/T) \text{ cm}^3 \text{ s}^{-1}$; this result derives from a compilation by Mitchell (1984), who in turn references a compilation by Westley (1980). Westley references yet a third compilation, that of Engleman (1976), who references a compilation of the Aerospace Corporation (Tunder et al. 1967), in which the value of the rate coefficient appearing in the UMIST compilation is stated to be an order-of-magnitude estimate. This estimate is most likely erroneous by more than an order of magnitude, because it would appear to be in grave conflict with the only known experimental work on the system – that of Graven & Long. Given the possible importance of reaction (2), we have

Send offprint requests to: E. Herbst,
e-mail: herbst@mps.ohio-state.edu

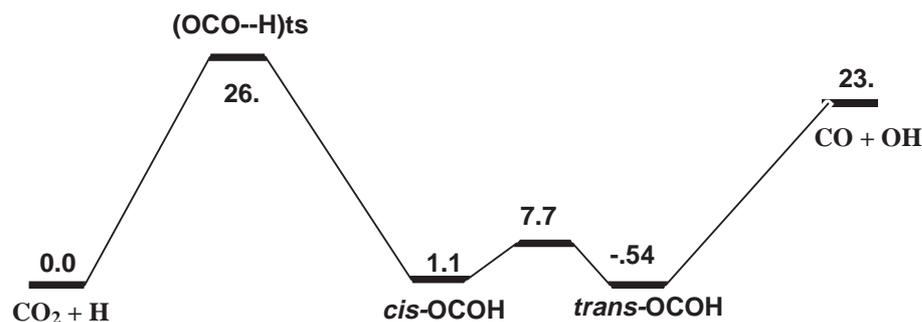


Fig. 1. CCSD(T)/6-311++G(3df, 2pd)//B3LYP/6-311+G(2d,p) lowest energy pathway for the reaction $\text{CO}_2 + \text{H} \rightarrow \text{CO} + \text{OH}$. Energies of stationary points are in kcal mol^{-1} ($1 \text{ kcal mol}^{-1} = 503.2 \text{ K}$). Zero point energies are included after scaling by a factor of 0.9613.

decided to study it via quantum chemical and dynamical methods. Our findings, to be reported below, show that the barrier for this reaction is very large, and its importance in interstellar chemistry very small except possibly in the case of large excitation of the reactants, thermal or otherwise. We have also studied reaction (1) in order to test the reliability of our approach.

2. Quantum chemical calculations

An extensive investigation was undertaken of the lowest doublet and singlet potential energy surfaces corresponding, respectively, to an H atom and H₂ molecule approaching CO₂. For that purpose, the density functional formalism (B3LYP functional; Becke 1993) was used in combination with a triple split-valence basis set to which diffuse orbitals were added together with polarization functions (namely 6-311+G(2d,p)). The B3LYP functional was chosen because it is known to be reliable for potential energy surface investigations; in particular it is known to give equilibrium geometries close to the experimental ones. If this functional is well designed for strong intramolecular interactions, however, it is not well designed for the weak intermolecular forces responsible for the existence of long-distance complexes (Zhang et al. 1997). Such complexes have been confirmed both theoretically and experimentally by Lester et al. (2000, 2001) in the CO₂ + H system.

The characters of the stationary points other than long-distance complexes located on these surfaces (either minimum energy points, for which all vibrational frequencies are real, or saddle points, characterized by one imaginary frequency) were confirmed by vibrational analysis done at the same B3LYP/6-311+G(2d,p) level. The structures corresponding to the saddle points are often referred to as transition states (ts). For accurate electronic energies, single point calculations were performed at the CCSD(T)/6-311++G(3df, 2pd) theoretical level using the B3LYP/6-311+G(2d,p) optimized geometries (hereafter CCSD(T)/6-311++G(3df, 2pd)//B3LYP/6-311+G(2d,p)). This is a coupled cluster singles and doubles method with a perturbative treatment of the triple excitations (Raghavachari et al. 1989), employing the

previous triple-zeta basis set to which extra sets of polarization functions as well as diffuse orbitals have been added. With such a basis set, we reach a flexibility in the single determinant representation that approaches the Hartree-Fock limit. All energies were corrected for zero-point energy (ZPE) contributions calculated at the B3LYP/6-311+G(2d,p) level and scaled by a factor of 0.9613 (Frisch et al. 1996). All the quantum chemical calculations of this study were performed by means of the Gaussian 98 package (Frisch et al. 1998).

The CCSD(T)/6-311++G(3df, 2pd)//B3LYP/6-311+G(2d,p) minimum energy pathways, or energy profiles, for reactions (1) and (2) are shown in Figs. 1 and 2, respectively. As can be seen, both reactions are calculated to be endothermic: CO₂ + H by 23 kcal mol⁻¹ (11 600 K) and CO₂ + H₂ by 9.2 kcal mol⁻¹ (4600 K). These exothermicities are in excellent agreement with experimental values (Lias et al. 1988). The energy profiles of both reactions show transition state structures, which appear as maxima along the minimum energy pathways although they actually correspond to saddle points in the multi-dimensional surfaces; these occur at 26 kcal mol⁻¹ (13 100 K) and 7.7 kcal mol⁻¹ (3870 K) for reaction (1) and at 113 kcal mol⁻¹ (56 900 K) for reaction (2). The energy profile for reaction (1) is in reasonable agreement with an earlier theoretical study (Schatz et al. 1987) and in very good agreement with the more recent study of Ducan & Miller (2000). This profile is more complex than that for reaction (2); following the major transition state formed by the collision of CO₂ and H, there are two intermediate structures with energy minima (so-called complexes) separated by a low-lying transition state. In addition to these features, weakly-bound linear OH...OC and OH...CO complexes are known to exist (Lester et al. 2000, 2001) as is the transition state connecting them to the stable *trans*-OCO-H minimum. These long-distance features were not searched for in our calculations because they have little effect on the rate of the CO₂ + H reaction. The energy of the dominant (rate-limiting) transition state for the CO₂ + H reaction is only slightly higher than that of the products, whereas the energy of the corresponding transition state for CO₂ + H₂ is much larger than the reaction endothermicity.

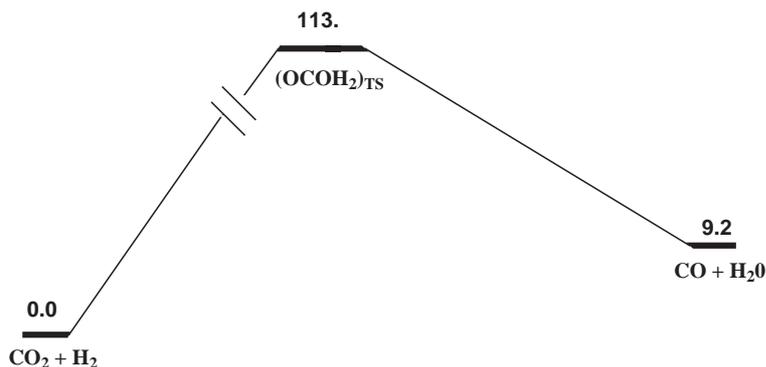


Fig. 2. CCSD(T)/6-311++G(3df, 2pd)//B3LYP/6-311+G(2d,p) lowest energy pathway for the reaction $\text{CO}_2 + \text{H}_2 \longrightarrow \text{CO} + \text{H}_2\text{O}$. Energies of stationary points are in kcal mol^{-1} ($1 \text{ kcal mol}^{-1} = 503.2 \text{ K}$). Zero point energies are included after scaling by a factor of 0.9613.

Table 1. Computed harmonic frequencies and rotational constants of major transition state structures.

Species	Harmonic frequencies ¹ (cm^{-1})	Rotational constants ² (GHz)
$(\text{OCO}\cdots\text{H})_{\text{TS}}$	$a' = 507, 871, 1245, 2104$ $1463i$ $a'' = 622$	238.78784 10.98235 10.49946
$(\text{OCO}\cdots\text{H}_2)_{\text{TS}}$	163, 343, 636, 757 826, 1170, 1867, 2705 $1457i$	85.142978 10.2786068 9.346272

¹ Harmonic frequencies have been calculated at the B3LYP/6-311+G(2d,p) level and scaled by 0.9613.

Group theoretical designations refer to the symmetry of the vibrational modes. $i = \sqrt{-1}$.

² Rotational constants have been calculated at the B3LYP/6-311+G(2d,p) level.

Since the vibrational frequencies and rotational constants of the major transition state structures are needed for rate calculations, these are listed in Table 1.

3. Rate coefficients

To calculate the thermal rate coefficient for a simple reaction in which the energy profile goes from reactants to products via a single transition state and no intermediate complex, we can use the “activated complex” theory (ACT; Weston & Schwarz 1972; Talbi & Herbst 2001; Herbst & Talbi 1998), which is more accurately referred to nowadays as the “transition state theory”, or TST. The reaction between CO₂ and H₂, reaction (2), is such a simple case. Its rate coefficient in the standard TST approximation is given by the equation

$$k_2 = (kT/h)R_{\text{trans}}R_{\text{rot}}R_{\text{vib}}R_{\text{elec}}\Gamma_{\text{t}}\exp(-E_{\text{ts}}/T) \quad (4)$$

where k is the Boltzmann constant, h is Planck’s constant, T is the temperature, E_{ts} is the energy in K of the transition state relative to the energy of reactants (with zero-point corrections), and the R ’s are ratios between partition functions of the transition state and of the reactants for translational, rotational, vibrational, and electronic modes (Weston & Schwarz 1972). A tunneling correction Γ_{t} also appears (Herbst 1996). All factors but

the exponential term can be lumped together as a pre-exponential factor $A(T)$.

The dominant term in the TST expression for reaction (2) is the exponential one because of the large size of E_{ts} : $113 \text{ kcal mol}^{-1}$ (56900 K). Thus, even at temperatures as high as 1200 K (the highest temperature mentioned by Doty et al. 2002), the very large negative value of the exponent ($-E_{\text{ts}}/T = -47$) renders the rate coefficient effectively zero whatever the value of the pre-exponential term. Nevertheless, we have calculated $A(T)$ to be $3.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 1000 K and $9.5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 2000 K .

To partially confirm our methods, we have used quantum chemical theory and the transition state method to estimate the rate coefficient for the well-studied reaction between CO₂ and H. Use of the TST approach (Eq. (4)) for this system yields an upper limit to the rate coefficient since the possibility that the complexes (see Fig. 1) redissociate into reactants is ignored. Because the energy of the products is lower than that of the major transition state, it is likely that the complexes will dissociate into products, so that the TST expression should yield a tight upper limit. Using the calculated energy for the major transition state as well as its vibrational frequencies and rotational constants (Fig. 1, Table 1), we obtain that the exponential term in the TST rate coefficient for the reaction between

CO₂ and H is $\exp(-13\,100/T)$ while the pre-exponential factor is $4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 300 K, $3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 1000 K, $4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 2000 K, and $5 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ at 3000 K. The agreement with the experimental values for CO₂ + H discussed in the Introduction is excellent.

4. Conclusions

We conclude that our results for reaction (2) – CO₂ + H₂ – show that this reaction plays no role in interstellar chemistry under ordinary conditions. The only circumstances under which reaction (2) could be invoked are (a) exceedingly high temperatures, and/or (b) non-thermal excitation of the reactants. The effects of internal excitation of reactants within the TST approximation have been discussed in some detail by Wagner & Graff (1987). For vibrational excitation, the major change is to replace the transition state energy in the exponent of Eq. (4) with an energy E' defined by the relation

$$E' = E_{\text{ts}} + \Delta\epsilon_v \quad (5)$$

where $\Delta\epsilon_v$ is the difference in vibrational energy between a specific vibrational state of the transition state and the excited vibrational state of reactants of interest; the states are adiabatically correlated with each other and are both labelled with quantum number v . For example, if we consider vibrational excitation of H₂, the mode of the transition state that correlates with this excitation is doubtless the highest frequency mode, occurring at 2705 cm⁻¹ (see Table 1). If this mode is designated by a , then

$$\Delta\epsilon_v = E_v(\text{ts}, a) - E_v(\text{H}_2). \quad (6)$$

Evaluation of $\Delta\epsilon_v$ shows that, at least in the adiabatic TST approximation, vibrational excitation of H₂ is not particularly efficient in increasing the rate coefficient k_2 because the two terms on the right-hand side of Eq. (6) are not greatly different from one another for any value of quantum number v . If we consider the first excited vibrational state as an example, we compute that $\Delta\epsilon_1 = -2100 \text{ K}$ so that E' is only 2100 K less than E_{ts} . For higher vibrational states of H₂, $\Delta\epsilon_v$ is undoubtedly more negative, but is still not large enough in an absolute sense to make E' sufficiently small to raise k_2 to a significant value. On the other hand, for large amounts of vibrational energy, the adiabatic treatment may be particularly poor since the density of vibrational states will be so high. Given the untested nature of the approximation for vibrational excitation, as well as similar approximations for other forms of non-thermal reactant energy, more detailed theoretical treatments and, preferably, experimental measurements of the rate coefficient for reaction (2) under non-thermal conditions are needed.

Acknowledgements. We thank the referee for his detailed comments, and S. Doty and A. Boonman for bringing this problem to our attention. The Astrochemistry Program at The Ohio State University is supported by The National Science Foundation (US). Parts of the calculations reported here were supported by the CINES (France); the support is gratefully acknowledged.

References

- Becke, A. D. 1993, *J. Chem. Phys.*, 98, 5648
 Boonman, A. M. S., van Dishoeck, E. F., Lahuis, F., Wright, C. M., & Doty, S. D. 2000, in *ISO Beyond the Peaks*, ed. A. Salama, M. F. Kessler, K. Leech, & Schulz, ESA-SP, 456, 67
 Charnley, S. B., & Kaufman, M. J. 2000, *ApJ*, 529, L111
 de Graauw, T., Whittet, D. C. B., Gerakines, P. A., et al. 1996, *A&A*, 315, 345
 Doty, S. D., van Dishoeck, E. F., van der Tak, F. F. S., & Boonman, A. M. S. 2002, *A&A*, submitted
 Ducan, T. V., & Miller, C. E. 2000, *J. Chem. Phys.*, 113, 5138
 Engleman, V. S. 1976, *Survey and Evaluation of Kinetic Data on Reactions in Methane/Air Combustions*. (Environmental Protection Agency Report), EPA-600/2-76-003
 Frisch, M. J., Trucks, G. W., & Cheeseman, J. R. 1996, in *Recent Developments and Applications of Modern Density Functional Theory, Theoretical and Computational Chemistry*, vol. 4, ed. J. Seminario (Amsterdam: Elsevier), 679
 Frisch, M. J., Trucks, G. W., Schlegel, H. B., et al. 1998, *Gaussian 98 (Revision A.5)* (Pittsburgh: Gaussian, Inc.)
 Gerakines, P. A., Whittet, D. C. B., Ehenfreund, P., et al. 1999, *ApJ*, 526, 1062
 Graven, W. M., & Long, F. J. 1954, *J. Am. Chem. Soc.*, 76, 2602
 Herbst, E. 1996, in *Atomic, Molecular, & Optical Physics Handbook*, ed. G. W. F. Drake (Woodbury, NY: AIP Press), 429
 Herbst, E., & Talbi, D. 1998, *A&A*, 338, 1080
 Lester, M. I., Pond, B. V., Anderson, D. T., Harding, L. B., & Wagner, A. F. 2000, *J. Chem. Phys.*, 113, 9889
 Lester, M. I., Pond, B. V., Marshall, M. D., et al. 2001, *Faraday Disc.*, 118, 373
 Le Teuff, Y. H., Millar, T. J., & Markwick, A. J. 2000, *A&AS*, 146, 157
 Lias, S., Bartmess, J. E., Liebman, J. F., et al. 1988, *J. Phys. Chem. Ref. Data*, vol. 17 (Supplement 1)
 Lissianski, V., Yang, H., Qin, Z., et al. 1995, *Chem. Phys. Lett.*, 240, 57
 Mitchell, G. F. 1984, *ApJ*, 287, 665
 Raghavachari, K., Trucks, G. W., Pople, J. A., & Head-Gordon, M. 1989, *Chem. Phys. Lett.*, 157, 479
 Schatz, G. C., Fitzcharles, M. S., & Harding, L. B. 1987, *Faraday Discuss. Chem. Soc.*, 84, 359
 Smith, I. W. M. 1988, *MNRAS*, 234, 1059
 Talbi, D., & Herbst, E. 2001, *A&A*, 376, 663
 Tsang, W., & Hampson, R. F. 1986, *J. Phys. Chem. Ref. Data*, 15, 1087
 Tunder, R., Mayer, S., Cook, E., & Schieler, L. 1967, *Aerospace Corp. Report No. TR-1001(9210-02)-1*, AD 813 485
 van Dishoeck, E. F. 1998, *Faraday Disc.*, 109, 31
 van Dishoeck, E. F., Helmich, F. P., de Graauw, T., et al. 1996, *A&A*, 315, 349
 Wagner, A. F., & Graff, M. M. 1987, *ApJ*, 317, 423
 Westley, F. 1980, *Table of recommended rate constants for chemical reactions occurring in combustion* (National Bureau of Standards, US) NSRDS-NBS 67
 Weston, Jr., R. E., & Schwarz, H. A. 1972, *Chemical Kinetics* (Englewood Cliffs, NJ: Prentice-Hall)
 Whittet, D. C. B., Gerakines, P. A., Tielens, A. G. G. M., et al. 1998, *ApJ*, 498, L159
 Zhang, Y., Pan, W., & Yang, W. 1997, *J. Chem. Phys.*, 107, 7921