JOURNAL OF THE CHEMICAL SOCIETY

Chemical Communications

Number 14
1990

Reaction of CS_2 with OH: a Quantum Chemical Study

S. Lunell,*[a] M.-B. Huang,[b] K. A. Sahetchian,[c] C. Chachaty,[d] and F. Zabel[e]

[a] *Department of Quantum Chemistry, Uppsala University, Box 518, S-751 20, Uppsala, Sweden*
[b] *Department of Modern Chemistry, University of Science and Technology of China, Hefei, Anhui, China*
[c] *Laboratoire de Chimie Générale, C.N.R.S. U.R.A. 870, Université P. et M. Curie, Tour 55, 4, Place Jussieu, F-75230 Paris Cedex 05, France*
[d] *IRDI/DESICP, Departement de Physico Chimie, C.E.N. Saclay, F-91191 Gif-sur-Yvette Cedex, France*
[e] *Physikalische Chemie, Universität-Gesamthochschule Wuppertal, 56 Wuppertal 1, West Germany*

Ab initio calculations on the reaction between carbon disulphide, CS_2, and an OH radical predict that an intermediary complex is formed with OH attached to the carbon atom, the reaction being exothermic without an energy barrier, while unimolecular decomposition of this complex into OCS and SH by proton rearrangement is found to be hindered by a very high potential energy barrier.

The atmospheric oxidation of CS_2 is of great importance since two potential oxidation products, OCS and SO_2, have a major environmental impact as greenhouse and pollutant gases. To understand this reaction is also important for understanding the roles of CS_2 in the global sulphur cycle. Oxidation of CS_2 in the atmosphere by reaction (1) is plausible. Laboratory studies on this reaction were started at least ten years ago, early experiments[1] suggesting the mechanism in reaction (2).

$$CS_2 + OH \rightarrow \text{products} \quad (1)$$

$$CS_2 + OH \rightarrow (CS_2OH)^* \rightarrow OCS + SH \quad (2)$$

Here, the CS_2OH adduct was considered as an intermediate. Later, the mechanism in reactions (3) and (4) was also proposed,[2] where M is a medium which absorbs excess energy released in the first step. CS_2OH is considered to be an intermediate in both the above mentioned mechanisms. The detailed structure of this intermediate, as well as the details of the reactions involved, are, however, not known.

$$CS_2 + OH + M \rightleftharpoons CS_2OH + M \quad (3)$$

$$CS_2OH + O_2 \rightarrow \text{products} \quad (4)$$

To gain some insight into these reactions, *ab initio* calculations have been performed. The calculations were carried out at the Hartree-Fock (UHF) level using the program GAUSSIAN 86.[3] A 3-21G basis[4] was employed in an overall scan of the energy hypersurface to find possible stable structures and transition states. Polarized 3-21G* and

Table 1. HF/3-21G* optimized geometries and total energies for the CS_2OH structures,[a] HF/3-21G results within parentheses [1 a.u. = 627.7 kcal mol^{-1}; 1 cal = 4.184 J; for notations see Figures 1 (a) and (b)].

Structure	(1)	(2)	(3)	(4)
R_1/Å	1.7277(1.7925)	1.5565(1.6202)	1.6165(1.6670)	1.6198(1.6751)
R_2/Å	1.6265(1.6755)	1.6091(1.7429)	1.7541(1.8291)	1.7564(1.8280)
R_3/Å	1.3417(1.3252)	1.6595(1.7349)	1.3458(1.3179)	1.3479(1.3169)
R_4/Å	0.9717(0.9729)	0.9716(0.9726)	1.3281(1.3553)	1.3231(1.3488)
α_1/°	123.1(123.2)	160.0(143.4)	124.8(124.4)	128.6(127.5)
α_2/°	125.4(125.7)	109.1(103.4)	112.7(111.8)	109.9(109.8)
α_3/°	112.6(113.3)	113.2(109.8)	97.1(97.9)	94.6(94.8)
ϕ_1/°	—	1.5(1.5)	—	—
ϕ_2/°	—	79.5(85.9)	—	—
E/a.u.	−903.97784 (−903.76871)	−903.93635 (−903.68745)	−903.95350 (−903.72879)	−903.95371 (−903.73025)

[a] Structures (**1**), (**3**), and (**4**) have a planar geometry and the electronic state $^2A'$, while structure (**2**) has a nonplanar geometry with the S(1) and H atoms above the C–S(2)–O plane.

Table 2. Relative energies (kcal mol^{-1}).

	CS_2 + OH	(1)	TS_1	(3)	TS_2	OCS + SH	(2)	(4)
HF/3-21G	36.7	10.6	high	35.6	41.0	0	61.6	34.7
HF/3-21G*	25.1	11.8	—	27.0	—	0	37.8	26.9
HF/6-311++G**	35.9	16.3	—	—	—	0	—	—
HF/6-311++G(2df,2pd)//HF/6-311++G**	36.6	17.8	—	—	—	0	—	—
HF/3-21G*, incl. BSSE correction	13.5	11.8	—	—	—	0	—	—
HF/6-311++G**, incl. BSSE correction	33.8	16.3	—	—	—	0	—	—
MP2/3-21G*//HF/3-21G*	33.7	20.0	—	—	—	0	—	—

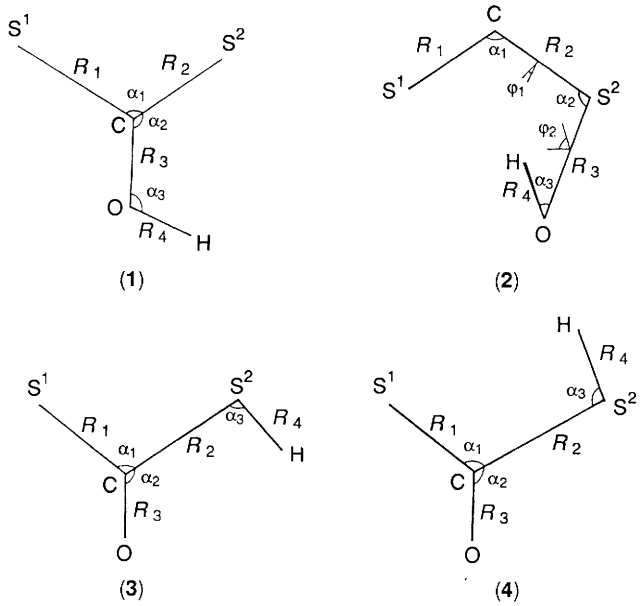

Figure 1. (a) Geometries and labelling for structures (**1**) and (**2**) of the CS_2OH system (possible structures of the product of the initial step). (b) Geometries and labelling for the structures (**3**) and (**4**) of the CS_2OH system [(**3**) is the structure of the product of the assumed second reaction step (proton transfer)].

6-311++G** bases[4] were used for refined optimizations of the stable structures which were identified in the 3-21G calculations.

S_2C–OH S–C–S–OH
(1) (2)

The CS_2OH adduct so far remains unobserved, but is important for the study of the whole reaction mechanism. Assuming that OH attacks the CS_2 molecule with its oxygen atom, two different structures, (**1**) and (**2**), are possible [see Figure 1(a)]. Optimized parameters and total energies for (**1**) and (**2**) are given in Table 1. Structure (**1**) is planar and (**2**) is nonplanar. Bonds involving sulphur are shorter in the HF/3-21G* calculations than in the HF/3-21G ones, because of the improved description given by the d functions on sulphur. Both C–S bonds are, however, much longer in (**1**) than in CS_2, where they were calculated as 1.58 and 1.54 Å, respectively, by HF/3-21G and HF/3-21G*. Frequency analyses confirm that both (**1**) and (**2**) correspond to energy minima in the potential energy surface. The HF/6-311++G** geometries differ only marginally from the 3-21G* ones, and are not reported.

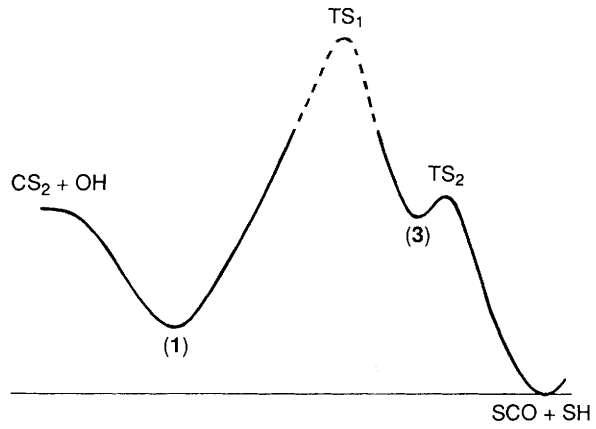

Figure 2. A schematic potential energy diagram for the considered reaction mechanism (see text).

Structure (**1**) was predicted to be much more stable than (**2**) by 51 kcal mol^{-1} in the HF/3-21G calculations and by 26 kcal mol^{-1} in the HF/3-21G* calculations. Therefore we conclude that structure (**1**), with OH attached to the carbon atom, should correspond to the product of the initial step in the reaction of CS_2 with OH. A set of HF/3-21G calculations indicate that there is no energy barrier for this reaction step (see Figure 2).

In order to study the energetics of this reaction, calculated energies of free CS_2 and OH were subtracted from the energy of CS_2OH (**1**) (see Table 2). A complication is that the 3-21G and 3-21G* results are likely to be heavily affected by basis set superposition errors (BSSE).[5] This is confirmed by the results in Table 2, where the BSSE has been estimated by calculating the energies of the free CS_2 and OH molecules in the complete basis of the adduct. It has, however, been shown that these types of 'counterpoise corrections' to results obtained in a small basis are of doubtful value,[6,7] and that the BSSE is better avoided by increasing the basis. The energetics of reaction (2) were therefore studied also at the HF/6-31++G** level and higher, where Table 2 shows that the BSSE is quite insignificant (2.1 kcal mol^{-1}). The predicted stabilization energy of 17—20 kcal mol^{-1} is in fair agreement with the experimental ΔH values of −8.7—13.9 kcal mol^{-1} for adduct formation,[2] considering the fact that all changes in vibrational and rotational energy are omitted, as well as the effects of electron correlation. A simple MP2/3-21G* calculation indicates that the latter may not be so important in this case (*cf.* Table 2), although this result should be viewed with care.

Since OCS is one of the observed products in the experiments,[2] the mechanism in reaction (5) for a possible further unimolecular decomposition of CS_2OH was examined, con-

sisting of two steps: the rearrangement of CS_2OH from (**1**) to (**3**) by means of a proton transfer from O to S(2) [see Figure 1(b)], and the cleavage of the C–S(2) bond in (**3**).

$$\underset{(\mathbf{1})}{CS_2OH} \rightarrow \underset{(\mathbf{3})}{CS_2OH} \rightarrow SH + OCS \qquad (5)$$

The optimized geometries and total energies of (**3**) and its rotational isomer (**4**) are given in Table 1 [also see Figure 1 (b)]. Both structures correspond to minima in the potential energy surface and have very similar total energies. In the present calculations, only (**3**) was considered.

The transition state (TS_2) between (**3**) and the final products in the suggested mechanism was located at the HF/3-21G level of accuracy, and it was predicted to be only 5.4 kcal mol^{-1} higher in energy than (**3**) at this level (see Table 2), a value which would be further reduced by electron correlation. Calculations for geometries around TS_2 indicate that the products from the cleavage of the C–S(2) bond in (**3**) are just the SH radical and the OCS molecule, not the ion pairs.

However, we failed to find the transition state (TS_1) between (**1**) and (**3**), and calculations on selected intermediate geometries between (**1**) and (**3**) indicated that TS_1 must be very high in energy. For the analogous rearrangement of the O_2COH radical, where the TS has a symmetric geometry since the corresponding structures '(**1**)' and '(**3**)' are equivalent, the barrier was in HF/3-21G calculations found to be as high as 52.8 kcal mol^{-1}. Even though electron correlation will lower this value, we consider it unlikely that this rearrangement occurs for either CS_2OH or O_2COH. Therefore the mechanism assumed in equation (5) does not appear very probable.

Figure 2 schematically illustrates the energy variation along the suggested reaction path. The first part of the curve (to the left of the first minimum) has been confirmed by our calculations, and the rest of the curve represents the proposed further reaction according to equation (5). The very high energy of TS_1 throws serious doubt on this reaction mechanism, our calculations suggesting that the reactions after the first reaction step can hardly occur without a catalyst. In this respect, the present results are in accord with experimental findings, indicating that oxygen is involved in the total reaction.[8,9]

This work was supported by the Swedish National Science Research Council (NFR). M.B.H. expresses his gratitude to the Swedish Institute for the award of a guest research scholarship.

Received, 9th February 1990; Com. 0/00606H

References

1 M. Kurylo, *Chem. Phys. Lett.*, 1978, **58**, 238.
2 A. J. Hynes, P. H. Wine, and J. M. Nicovich, *J. Phys. Chem.*, 1988, **92**, 3846.
3 GAUSSIAN 86, M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. DeFrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fluder, and J. A. Pople, Carnegie-Mellon Quantum Chemistry Publishing Unit, Pittsburgh, PA, 1984.
4 See, *e.g.*, W. J. Hehre, L. Radom, P. v. R. Schleyer, and J. A. Pople, '*Ab Initio* Molecular Orbital Theory,' Wiley-Interscience, New York, 1986.
5 S. F. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553.
6 D. W. Schwenke and D. G. Truhlar, *J. Chem. Phys.*, 1985, **82**, 2418.
7 M. J. Frisch, J. E. DelBene, J. S. Binkley, and H. F. Schaefer III, *J. Chem. Phys.*, 1986, **84**, 2279.
8 B. M. R. Jones, J. P. Burrows, R. A. Cox, and S. A. Penkett, *Chem. Phys. Lett.*, 1982, **88**. 372.
9 I. Barnes, K. H. Becker, E. H. Fink, A. Reiner, F. Zabel, and H. Niki, *Int. J. Chem. Kinet.*, 1983, **15**, 631.