24 August 2001

ELSEVIER

Chemical Physics Letters 344 (2001) 310–316

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

Low temperature rate coefficients for the reactions of CN and C_2H radicals with allene ($CH_2{=}C{=}CH_2$) and methyl acetylene ($CH_3C{\equiv}CH$)

David Carty, Valery Le Page, Ian R. Sims *, Ian W.M. Smith

School of Chemistry, The University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

Received 5 April 2001; in final form 22 May 2001

Abstract

Using a continuous flow CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme or Reaction Kinetics in Uniform Supersonic Flow) apparatus, rate coefficients have been measured for the reactions of the cyanogen (CN) and ethynyl (C_2H) radicals with allene ($CH_2{=}C{=}CH_2$) and methyl acetylene ($CH_3C{\equiv}CH$) at temperatures from 295 down to 15 K for the reactions of CN and down to 63 K for those of C_2H. All four reactions occur at rates close to the collision-determined limit. The results are compared with those obtained earlier for the reactions of other alkenes and alkynes, and, in the accompanying Letter by Vakhtin et al., with results for $C_2H + CH_2{=}C{=}CH_2$ and $C_2H + CH_3C{\equiv}CH$ obtained at 103 K using a pulsed Laval apparatus. The implications of these latest results for the chemistry of interstellar clouds and planetary atmospheres are discussed.

1. Introduction

Over the past decade, rate coefficients for almost 40 elementary reactions between electrically neutral species have been measured at temperatures as low as 13 K [1]. These experiments employ continuous flow CRESU (Cinétique de Réaction en Ecoulement Supersonique Uniforme or Reaction Kinetics in Uniform Supersonic Flow) apparatuses in Rennes and Birmingham, in which expansion of a gas mixture through a Laval nozzle generates a cold, uniform and relatively dense supersonic flow of gas downstream from the nozzle, with a temperature which is defined by the design of the convergent–divergent nozzle. The results of the experiments, which demonstrate that many neutral–neutral reactions can remain fast down to very low temperatures, have led to a major re-evaluation of the processes that may contribute to the chemistry leading to molecular formation in dense interstellar clouds [2].

Amongst the reactions whose kinetics have been studied down to very low temperatures are those of the CN [3–5] and C_2H radicals [6]. In 1993, Smith and Sims [7] proposed that the reactions of these radicals with alkynes could provide a route to the synthesis of the cyanopolyynes, which are found widely in interstellar environments. This proposal was based on (a) the rapidity of the reactions of CN and C_2H with alkynes at room temperature, (b) early CRESU measurements that demonstrated that the reaction of CN radicals

* Corresponding author. Fax: +44-121-414-4426.
E-mail address: i.r.sims@bham.ac.uk (I.R. Sims).

0009-2614/01/$ - see front matter
PII: S0009-2614(01)00682-0

with C_2H_2 occurred at essentially the collision-limited rate below 100 K, and (c) the likelihood that CN and C_2H would react with a given alkyne at similar rates because the two radicals are isoelectronic. Later measurements of the rate coefficients for the reactions of C_2H with C_2H_2, C_2H_4 and C_3H_6 [6] confirmed that reactions of C_2H with unsaturated hydrocarbons occur at rates comparably fast to those of CN radicals. Moreover, modelling calculations [8,9] have shown that neutral chemistry is important in producing cyanopolyynes under the conditions prevalent in dense interstellar clouds.

Chastaing et al. [6] added to the original arguments of Smith and Sims [7] by pointing out that the rates of addition of a given free radical to unsaturated hydrocarbons have been correlated to the ionisation energy of the unsaturated species [10]. As the higher alkenes and alkynes have lower ionisation energies than C_2H_4 and C_2H_2 [11], respectively, then it is to be expected that higher alkenes and alkynes will react at least as fast as C_2H_4 and C_2H_2 with CN and C_2H radicals. The measurements on the reactions of CN and C_2H with $CH_2{=}C{=}CH_2$ and $CH_3C{\equiv}CH$ that are reported in the present Letter provide a partial test of this proposal.

A second reason for the present measurements is to extend a comparison of the rates of the same reactions that are measured in a continuous flow CRESU apparatus with those obtained in an apparatus that uses a pulsed Laval nozzle. A comparison for reactions of OH radicals has already been published [12]; the Letter accompanying this one [13] reports rate coefficients for the reactions of C_2H with C_2H_2, O_2, $CH_2{=}C{=}CH_2$ and $CH_3C{\equiv}CH$ at 103 K. These data are compared with earlier measurements from our laboratory [6] on the first two of these reactions and our present results for $C_2H + CH_2{=}C{=}CH_2$ and $C_2H + CH_3C{\equiv}CH$.

2. Experimental

Rate coefficients have been measured for the reactions of CN and C_2H with $CH_2{=}C{=}CH_2$ and $CH_3C{\equiv}CH$ at several temperatures between 294 and 15 K, in the case of the reactions of CN, and 296 and 63 K, in the case of the reactions of C_2H. A full description of the Birmingham CRESU apparatus has been given elsewhere [14]. Furthermore, the methods used to study the kinetics of these reactions of CN and C_2H closely follow those used previously [3–6].

However, in contrast with earlier experiments where the photolysis of NCNO was used to generate CN radicals, in the present experiments ICN was photolysed at 266 nm with the fourth harmonic output of a Nd:YAG laser (Spectron Lasers). A fraction of the carrier gas flow was passed over crystals of ICN before this flow of gas entered the gas reservoir upstream of the Laval nozzle. Photodissociation of ICN at this wavelength produces CN radicals that are overwhelmingly in the $v = 0$ level of the $X^2\Sigma^+$ ground vibronic state but over a wide range of rotational levels [15]. CN radicals were detected by exciting them in the (0,0) band of the CN ($A^2\Sigma^+ - X^2\Sigma^+$) system at ~388 nm, and observing the fluorescence in the (0,1) band at ~420 nm through a narrow band interference filter centred at ~420 nm with a 10 nm FWHM bandwidth. Kinetic decays were observed by recording the variation in the laser-induced fluorescence (LIF) signal as a function of the time delay between the pulses from the photolysis and probe lasers. These traces of LIF signal versus time delay were fitted to single exponential functions, the fit being started at time delays sufficient to allow for rotational relaxation. This procedure yielded pseudo-first-order rate coefficients related to the rate of loss of CN radicals.

C_2H radicals were generated by pulsed laser photolysis of C_2H_2 at 193 nm produced from transitions in ArF in one of three excimer lasers (Lambda Physik, Compex 102, Compex 202 or LPX 210i) operating with a pulse frequency of 10 Hz (Compex 102 and 202) and 30 Hz (LPX 210i) and a pulse duration of ~10 ns. The progress of C_2H reactions was monitored by observing chemiluminescence from CH ($A^2\Delta^+$), which is formed as a minor product of the reaction between C_2H and O_2 [16]. Details of this method and a discussion of possible complications are discussed at length by Chastaing et al. [6]. One of its disadvantages is that, to study any reaction of C_2H, it is

necessary to have both C_2H_2 and O_2 present, one as the photochemical precursor of the radicals and the other to generate the chemiluminescent marker, CH ($A^2\Delta^+$), as well as any other reagent such as allene or methyl acetylene. The 'background rate', i.e., that with no allene or methyl acetylene present, is substantial and means that relatively large concentrations of any third reagent must be added in order to change the first-order decay rates appreciably. In the present experiments, reliable kinetic measurements could not be made on the $C_2H + CH_2{=}C{=}CH_2$ and $C_2H + CH_3C{\equiv}CH$ reactions below 63 K because at the concentrations of allene and methyl acetylene needed to accelerate the rate of removal of C_2H over the background rate, there was significant loss of species due to the formation of dimers and higher complexes of the three molecules present.

3. Results

Second-order rate coefficients (k) for a given reaction were obtained by measuring pseudo-first-order rate coefficients (k_{1st}) for the disappearance of the radical, by the methods described in the previous section, for several ($\sim$10) concentrations of C_3H_4 ($CH_2{=}C{=}CH_2$ or $CH_3C{\equiv}CH$) and then plotting k_{1st} against $[C_3H_4]$. The gradient of these lines yields the value of k appropriate to the particular reagents and the selected temperature. Using different nozzles, measurements were made at several temperatures on each of the four reactions.

Our results are summarised in Table 1a–d and Figs. 1 and 2. In Fig. 1 the temperature-dependence of the rate coefficients for the reaction of CN and C_2H radicals with $CH_2{=}C{=}CH_2$ are displayed on a log–log plot of $k/10^{-10}$ cm^3 molecule^{-1} s^{-1} versus T/K. Fig. 2 shows the corresponding data for the reactions of the CN and C_2H radicals with $CH_3C{\equiv}CH$. Standard errors from the second-order plots have been multiplied by the appropriate Student's t-factor for 95% confidence limits. This corresponds to the statistical error. In addition, some systematic errors may have arisen from, for example, inaccuracies in the calibration of flow controllers or in the determination of the total gas density, but it is estimated that these errors are unlikely to exceed 10%. This estimate has been combined with the 95% confidence limits for statistical error in Table 1a–d and in Figs. 1 and 2.

In all four cases, the variation of the rate coefficient with temperature is slight. Indeed, for both reactions of the CN radical, differences between the rate coefficients for $CH_2{=}C{=}CH_2$ and $CH_3C{\equiv}CH$ are negligible, as are their temperature-dependences. For astrochemical modelling purposes, we recommend that a temperature independent value of $k = (4.1 \pm 0.5) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} is used. For both reactions of the C_2H radical, the rate coefficients show a negative dependence on temperature. Non-linear least squares fits of our data to the expression $k = A(T/298\ \mathrm{K})^n$ in the range $T = 63$–296 K gave the following results:

C_2H + allene :

$$k = (2.0 \pm 0.6) \times 10^{-10}(T/298\ \mathrm{K})^{-(0.4\pm0.3)}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

C_2H + methyl acetylene :

$$k = (2.1 \pm 1.6) \times 10^{-10}(T/298\ \mathrm{K})^{-(0.3\pm0.7)}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

Average absolute statistical deviations over the range of experiments were 0.1 and 0.3, respectively, in units of 10^{-10} cm^3 molecule^{-1} s^{-1}. Based on previous measurements of radical-unsaturated hydrocarbon molecule reactions [5,6,17–19] it is unlikely that the observed negative temperature-dependence will continue to temperatures significantly below our experimental range. We therefore recommend for astrochemical models of dense interstellar clouds, where the temperature is usually in the range 10–100 K, a temperature independent value of $k = (3 \pm 1) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} for both reactions.

4. Discussion

The Letter accompanying this one reports the measurement of rate coefficients for the reactions of C_2H radicals with $C_2H_2, O_2, CH_2{=}C{=}CH_2$ and $CH_3C{\equiv}CH$ at 103 K [13]. Cooling to this temperature is achieved using a pulsed Laval nozzle.

Table 1
Rate coefficients k for the reactions:

T/K	M	$[M]/10^{16}$ (molecule cm^{-3})	Range of $[C_3H_4]/10^{14}$ (molecule cm^{-3})	No. of points	$k/10^{-10}$ (cm^3 molecule^{-1} s^{-1})
(a) *CN radicals with allene*					
294	Ar	8.56	0.00–1.65	11	3.9 ± 0.4[a]
200	N_2	5.83	0.00–4.65	11	4.3 ± 0.5
112	Ar	2.79	0.00–2.58	12	4.5 ± 0.5
54	Ar	5.37	0.00–5.31	11	4.0 ± 0.5
27	He	4.65	0.40–3.97	10	3.9 ± 0.6
15	He	5.05	0.00–0.86	9	4.4 ± 1.1
(b) *CN radicals with methyl acetylene*					
294	Ar	8.56	0.00–1.58	11	4.0 ± 0.4
200	N_2	5.83	0.00–4.53	11	4.3 ± 0.5
112	Ar	2.79	0.00–2.52	11	4.4 ± 0.5
54	Ar	5.37	0.00–5.19	12	3.5 ± 0.4
27	He	4.65	0.39–3.88	10	3.6 ± 0.7
15	He	5.05	0.00–1.26	8	3.8 ± 0.7

T/K	M	$[M]/10^{16}$ (molecule cm^{-3})	$[C_2H_2]/10^{13}$ (molecule cm^{-3})	$[O_2]/10^{14}$ (molecule cm^{-3})	Range of $[C_3H_4]/10^{14}$ (molecule cm^{-3})	No. of points	$k/10^{-10}$ (cm^3 molecule^{-1} s^{-1})
(c) *C_2H radicals with allene*							
296	Ar	23.0	30.7	38.4	1.1–11.0	7	1.8 ± 0.3
149	He	1.42	2.53	2.12	0.2–2.1	9	2.8 ± 0.3
112	Ar	2.71	8.79	6.46	0.2–2.5	10	2.9 ± 0.3
63	He	2.03	4.19	4.37	0.1–1.5	10	3.5 ± 0.4
(d) *C_2H radicals with methyl acetylene*							
296	Ar	24.0	32.1	40.2	1.1–7.9	10	1.7 ± 0.3
149	He	1.42	2.33	1.95	0.2–1.9	10	2.9 ± 0.3
112	Ar	2.71	8.80	6.46	0.2–2.2	11	2.9 ± 0.3
63	He	2.03	4.19	4.37	0.1–1.4	10	2.9 ± 0.3

[a] Errors (here and throughout the tables) are quoted at the 95% confidence limit, and include a 10% contribution from possible systematic error.

Results for the reactions with C_3H_4 isomers are shown in Figs. 1 and 2. The results for all four of these reactions are in satisfactory agreement with those obtained using our continuous flow CRESU apparatus and reported in this Letter and previously [6].

The slightly smaller rate coefficients found for the reactions of C_2H compared with the corresponding ones for reactions of CN is consistent with what has been found before for the reactions of CN and C_2H with C_2H_4 and C_2H_2 [6]. There have been no previous measurements of low temperature rate coefficients for the reactions of CN with $CH_2{=}C{=}CH_2$ and $CH_3C{\equiv}CH$. As Fig. 1 shows, our results are consistent with rate coefficients determined by Lin and co-workers at room temperature and above [20]. For the reactions of C_2H with $CH_2{=}C{=}CH_2$ and $CH_3C{\equiv}CH$, rate coefficients have been determined at temperatures down to 155 K by Hoobler and Leone [21]. These data are also shown on Figs. 1 and 2. As with our results, they found little difference in the values of k for the two isomers of C_3H_4. Moreover, their data for these two reactions are reasonably consistent with ours.

Our experiments measure only the total rate of removal of the radical species (CN, C_2H) by the C_3H_4 reactants. There have been no studies of the products of these reactions at the low temperatures or collision energies appropriate to dense inter-

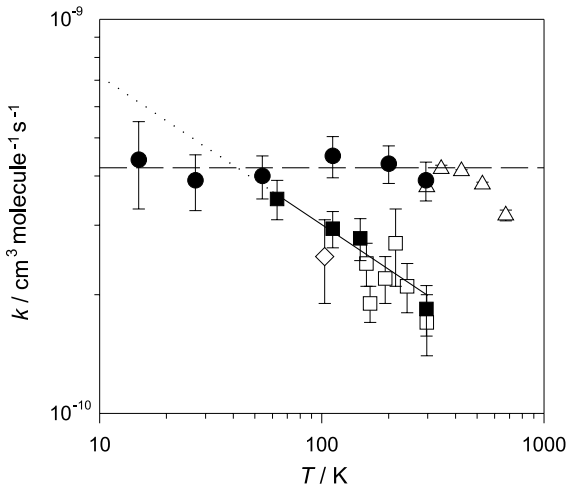

Fig. 1. Rate coefficients k for the reactions of CN and C_2H radicals with allene plotted on a log–log scale against temperature. The filled symbols show the results of this work: (●) denoting rate coefficients for CN + allene; and (■) denoting rate coefficients for C_2H + allene. For the CN + allene reaction, the horizontal dashed line represents our recommendation for the rate coefficient, $k = 4.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} and (△) shows the results of Butterfield et al. over the range $T = 297$–673K [20]. For the C_2H + allene reaction, (□) show the results of Hoobler and Leone over the range $T = 159$–297 K [21] and (◇) is the result of Vakhtin et al. from the accompanying Letter [13]. The solid line shows the result of a non-linear least-squares fit to our C_2H + allene data giving $k = 2.0 \times 10^{-10}$ $(T/298\ \mathrm{K})^{-0.4}$ cm^3 molecule^{-1} s^{-1} with an average absolute statistical deviation of 0.1×10^{-10} cm^3 molecule^{-1} s^{-1} over the range of experiments. The dotted line (· · ·) represents the extrapolation of this fit below the lowest temperature at which data were obtained.

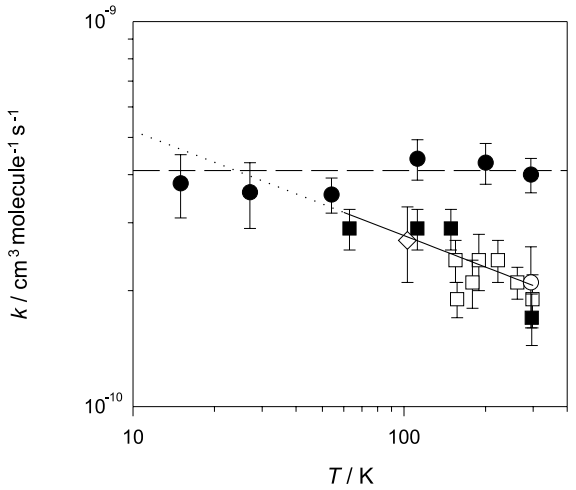

Fig. 2. Rate coefficients k for the reactions of CN and C_2H radicals with methyl acetylene plotted on a log–log scale against temperature. The filled symbols show the results of this work: (●) denoting rate coefficients for CN + methyl acetylene; and (■) denoting rate coefficients for C_2H + methyl acetylene. For the CN + methyl acetylene reaction, the horizontal dashed line represents our recommendation for the rate coefficient, $k = 4.1 \times 10^{-10}$ cm^3 molecule^{-1} s^{1} and (○) shows the room temperature result of Sayah et al. [29]. For the C_2H + methyl acetylene reaction, (□) show the results of Hoobler and Leone over the range $T = 155$–298 K [21] and (◇) is the result of Vakhtin et al. from the accompanying Letter [13]. The solid line shows the result of a non-linear least-squares fit to our C_2H + methyl acetylene data giving $k = 2.1 \times 10^{-10}$ $(T/298\ \mathrm{K})^{-0.3}$ cm^3 molecule^{-1} s^{-1} with an average absolute statistical deviation of 0.3×10^{-10} cm^3 molecule^{-1} s^{-1} over the range of experiments. The dotted line (· · ·) represents the extrapolation of this fit below the lowest temperature at which data were obtained.

stellar clouds or the atmospheres of planets such as Titan (~0.1–1 kJ mol^{-1}), and quantitative product branching ratios are unavailable at any temperature. However, crossed-molecular beam measurements have been performed at much higher collision energies (in the range 20–40 kJ mol^{-1}) by Lee, Kaiser and co-workers, coupled in most cases with potential energy surface calculations [22–25]. In all cases, they concluded that the barrier-free addition of the radical CN or C_2H followed by loss of an H-atom is either the only or a major pathway. For CN + allene, cyanoallene ($H_2C{=}C{=}CHCN$) was inferred as the major product [22], whereas for CN + methyl acetylene, both cyanopropyne ($CH_3C{\equiv}CCN$) and cyanoallene were observed [22,23]. The C_2H + methyl acetylene reaction is found at a collision energy of 38.8 kJ mol^{-1} to yield mainly methyl diacetylene ($CH_3C{\equiv}CC{\equiv}CH$), along with the minor product ethynyl allene ($H_2C{=}C{=}CHC_2H$) [24].

In Table 2 we list the rate coefficients at 50 K for the reactions of CN and C_2H with alkenes and alkynes that can be inferred from the present and previous [5,6] CRESU experiments. In all cases, the reaction is rapid with rate coefficients close to the collision-determined limit. The rate coefficients for the C_2H reactions are consistently smaller, by about a factor of 2, than those for CN. Table 2 also gives the ionisation energies of the unsaturated hydrocarbons including those for the

Table 2
Comparison of rate coefficients for the reactions of CN and C_2H radicals with alkenes and alkynes at $T = 50$ K, estimated from this work, that of Sims et al. [5] and that of Chastaing et al. [6]. Ionisation energies for the unsaturated hydrocarbons are also listed [11]

	$k_{CN}(T \approx 50\ K)/10^{-10}$ (cm^3 $molecule^{-1}$ s^{-1})	$k_{C_2H}(T \approx 50\ K)/10^{-10}$ (cm^3 $molecule^{-1}$ s^{-1})	Ionisation energy (eV)
HC≡CH	4.7	1.9	11.40
$CH_3C{\equiv}CH$	4.1	3.6	10.36
$H_2C{=}CH_2$	4.9	2.3	10.51
$CH_3CH{=}CH_2$	–	3.4	9.73
$CH_2{=}C{=}CH_2$	4.1	3.9	9.69
HC≡C–C≡CH	–	–	10.18
HC≡C–CC–C≡CH	–	–	9.5
HC≡CCN	–	–	11.64

polyynes C_4H_2 and C_6H_2, for which no low temperature kinetic data are available but which may be synthesised in interstellar clouds by reactions of C_2H radicals with smaller species:

$$C_2H + C_mH_n \rightarrow C_{m+2}H_n + H$$

and may be converted to cyanopolyynes by reaction with CN radicals:

$$CN + C_mH_n \rightarrow C_mH_{n-1}CN + H$$

as proposed by Smith and Sims [7]. Seki et al. have measured a room temperature rate coefficient for $CN + C_4H_2$ of $(4.2 \pm 0.2) \times 10^{-10}$ cm^3 $molecule^{-1}$ s^{-1} [26], and as C_4H_2 and C_6H_2 both have lower ionisation energies than C_2H_2 it is likely that they react at low temperatures with both CN and C_2H radicals at rates at least comparable to those for the reactions of C_2H_2. More recently, Fukuzawa et al. [27] have performed ab initio quantum calculations on the reactions of C_2H and CN with polyynes, and concluded that these reactions proceed without barriers, and, under the cold conditions of molecular clouds, lead exclusively to the products shown above.

Our results indicate that reactions of CN and C_2H with unsaturated hydrocarbons occur rapidly at low temperatures and should be included in chemical models of dense interstellar clouds and possibly in those of other astrophysical environments, such as the atmosphere of Titan. An interesting question that remains unresolved is whether CN and C_2H radicals react rapidly at low temperatures with cyanopolyynes themselves. Halpern and co-workers [28] have measured the room temperature rate coefficient for the reaction of CN with cyanoacetylene (HC≡CCN) and found it to be $(1.70 \pm 0.08) \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. They also inferred that it is likely that this reaction has a small activation energy (~6 kJ mol^{-1}). If they are correct, then this reaction would be too slow to play a significant role in the chemistry of dense interstellar clouds where the temperature is usually $\leqslant 50$ K. We note (see Table 2) that the ionisation energy of HC≡CCN is higher than that for C_2H_2 so the existence of a small activation energy for this reaction would not be inconsistent with the correlation of rates with ionisation energies that has been used to predict fast rates at low temperatures for the reactions of CN and C_2H with higher alkynes. Measurements of rate coefficients for these reactions at low temperatures are sorely needed.

Acknowledgements

We are grateful to EPSRC for substantial research grants to construct and extend the CRESU apparatus in Birmingham and for support of this work by the European Commission through a TMR Research Network grant, contract FMRX-CT97-0132 (DG12-MIHT), for research on Astrophysical Chemistry. DC also thanks EPSRC for the award of a research studentship.

References

[1] I.W.M. Smith, B.R. Rowe, Acc. Chem. Res. 33 (2000) 261.
[2] E. Herbst, Ann. Rev. Phys. Chem. 46 (1995) 27.

[3] I.R. Sims, J.L. Queffelec, A. Defrance, C. Rebrion-Rowe, D. Travers, P. Bocherel, B.R. Rowe, I.W.M. Smith, J. Chem. Phys. 100 (1994) 4229.
[4] I.R. Sims, J.L. Queffelec, A. Defrance, C. Rebrion-Rowe, D. Travers, B.R. Rowe, I.W.M. Smith, J. Chem. Phys. 97 (1992) 8798.
[5] I.R. Sims, J.L. Queffelec, D. Travers, B.R. Rowe, L.B. Herbert, J. Karthäuser, I.W.M. Smith, Chem. Phys. Lett. 211 (1993) 461.
[6] D. Chastaing, P.L. James, I.R. Sims, I.W.M. Smith, Faraday Discuss. (1998) 165.
[7] I.W.M. Smith, I.R. Sims, J. Chem. Soc. Faraday Trans. 89 (1993) 2166.
[8] E. Herbst, H.H. Lee, D.A. Howe, T.J. Millar, Mon. Not. Roy. Astron. Soc. 268 (1994) 335.
[9] R.P.A. Bettens, H.H. Lee, E. Herbst, Astrophys. J. 443 (1995) 664.
[10] E. Martinez, B. Cabanas, A. Aranda, J. Albaladejo, R.P. Wayne, J. Chem. Soc.-Faraday Trans. 93 (1997) 2043.
[11] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 17 (1988) 1.
[12] A.B. Vakhtin, D. Heard, I.W.M. Smith, S.R. Leone, J. Phys. Chem. 2001, in press.
[13] A.B. Vakhtin, D. Heard, I.W.M. Smith, S.R. Leone, Chem. Phys. Lett. 2001, accompanying paper, in press.
[14] P.L. James, I.R. Sims, I.W.M. Smith, M.H. Alexander, M.B. Yang, J. Chem. Phys. 109 (1998) 3882.
[15] W.H. Fisher, R. Eng, T. Carrington, C.H. Dugan, S.V. Filseth, C.M. Sadowski, Chem. Phys. 89 (1984) 457.
[16] K. Devriendt, H. VanLook, B. Ceursters, J. Peeters, Chem. Phys. Lett. 261 (1996) 450.
[17] I.R. Sims, in: R.G. Compton, G. Hancock (Eds.), Research in Chemical Kinetics, Blackwell Science, Oxford, 1997, p. 121.
[18] A. Canosa, I.R. Sims, D. Travers, I.W.M. Smith, B.R. Rowe, Astron. Astrophys. 323 (1997) 644.
[19] I.R. Sims, I.W.M. Smith, P. Bocherel, A. Defrance, D. Travers, B.R. Rowe, J. Chem. Soc.-Faraday Trans. 90 (1994) 1473.
[20] M.T. Butterfield, T. Yu, M.C. Lin, Chem. Phys. 169 (1993) 129.
[21] R.J. Hoobler, S.R. Leone, J. Phys. Chem. A 103 (1999) 1342.
[22] N. Balucani, O. Asvany, L.C.L. Huang, Y.T. Lee, R.I. Kaiser, Y. Osamura, H.F. Bettinger, Astrophys. J. 545 (2000) 892.
[23] L.C.L. Huang, N. Balucani, Y.T. Lee, R.I. Kaiser, Y. Osamura, J. Chem. Phys. 111 (1999) 2857.
[24] R.I. Kaiser, C.C. Chiong, O. Asvany, Y.T. Lee, F. Stahl, P.V. Schleyer, H.F. Schaefer, J. Chem. Phys. 114 (2001) 3488.
[25] F. Stahl, P.V. Schleyer, H.F. Bettinger, R.I. Kaiser, Y.T. Lee, H.F. Schaefer, J. Chem. Phys. 114 (2001) 3476.
[26] K. Seki, M. Yagi, M.Q. He, J.B. Halpern, H. Okabe, Chem. Phys. Lett. 258 (1996) 657.
[27] K. Fukuzawa, Y. Osamura, H.F. Schaefer, Astrophys. J. 505 (1998) 278.
[28] J.B. Halpern, G.E. Miller, H. Okabe, Chem. Phys. Lett. 155 (1989) 347.
[29] N. Sayah, X.C. Li, J.F. Caballero, W.M. Jackson, J. Photochem. Photobiol. A-Chem. 45 (1988) 177.