

# The reactions of the highly polar ion $\text{ArD}_3^+$ with $\text{C}_3\text{H}_8$ and $\text{C}_4\text{H}_{10}$

C. Praxmarer, A. Hansel, W. Lindinger\*

*Institut für Ionenphysik, Universität Innsbruck, Technikerstr. 25, A-6020 Innsbruck, Austria*

Received 10 July 1996; accepted 16 July 1996

## Abstract

A Selected Ion Flow Drift Tube (SIFDT) operated at 300 K with helium buffer gas has been used to obtain rate coefficients for the reactions of the highly polar ion  $\text{ArD}_3^+$  with  $\text{C}_3\text{H}_8$  and  $\text{C}_4\text{H}_{10}$ . The rate coefficients,  $k(\text{C}_3\text{H}_8) = (1.46 \pm 0.15) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  and  $k(\text{C}_4\text{H}_{10}) = (1.49 \pm 0.15) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  are higher than the respective Langevin limiting values  $k_L(\text{C}_3\text{H}_8) = 1.24 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  and  $k_L(\text{C}_4\text{H}_{10}) = 1.32 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  by 18 and 13 percent, respectively, an effect which is quantitatively explained on the basis of the interaction between the ion-dipole and the induced dipole of the neutral reactants.

**Keywords:** Reactions of  $\text{ArD}_3^+$ ; Polar ions; Ion-dipole/induced dipole interaction

## 1. Introduction

At thermal energies the ion-induced dipole interaction governs the formation of collision complexes between ions and non-polar neutrals. The rate coefficients for these complex formations, the so-called Langevin limiting values,  $k_L$ , have the temperature-independent values [1]

$$k_L = 2\pi e \left( \frac{\alpha}{m_r} \right)^{1/2}, \quad (1)$$

which are typically  $\sim 1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ .  $\alpha$  is the polarizability of the neutral reactant and  $m_r$  the reduced mass of the reaction partners. For many ion–neutral reactant pairs, the actual reaction proceeds with a rate coefficient equal to that of the Langevin complex formation,  $k_L$ . Especially in the case of a vast amount of proton transfer reactions, the measured thermal rate coefficients,  $k$ , agree, within experimental uncertainty, quite

well with the corresponding Langevin values,  $k_L$ . This means that most of these reactions have a reaction probability equal to unity.

Rakshit [2] and later on Smith et al. [3] have observed that the highly polar ion  $\text{ArH}_3^+$  reacts with various non-polar neutrals with rate coefficients which are distinctly larger than the corresponding Langevin limiting values,  $k_L$ . These significantly larger values of the rate coefficient of the  $\text{ArH}_3^+$  reactions than  $k_L$  were attributed by Smith et al. [3] to the interaction of the dipole moment of the ion with the quadrupole moment of the neutrals. However, extensive investigations by Praxmarer et al. [4] including reactions of  $\text{ArH}_3^+$  with both polar and non-polar neutrals (including several with and without quadrupole moments, respectively), indicate that it is predominantly the interaction between the ion-dipole and the induced dipole of the neutral reactant that causes the increase of the measured rate coefficients above  $k_L$  in the case of non-polar neutrals. In the case of polar neutrals

\* Corresponding author.

an additional interaction between the ion-dipole and the neutral-permanent dipole may also be of significant influence. The results of Praxmarer et al. [4] are in agreement with calculations [4] of rate coefficients based on an ion–neutral interaction potential of the form

$$V_{\text{eff}} = \frac{bE}{R^2} - \frac{\alpha e^2}{R^2} - \frac{\mu_i^2 \alpha}{R^6}, \quad (2)$$

which extends the effective potential on which the Langevin model is based [5] by the term  $-\mu_i^2 \alpha / R^6$ , taking account of the ion–permanent-dipole interaction with the induced dipole of the neutral reactant. Here  $\mu_i$  is the permanent dipole moment of the ion (which is  $\sim 8$  D in the case of the ion  $\text{ArH}_3^+$  [6,7]). The inclusion of this dipole-induced dipole term increases the theoretical thermal capture rate coefficient  $k_{\text{L,ID}}$  above  $k_{\text{L}}$ , as shown in Fig. 1. As has already been discussed by Su and Bowers [8] and by Clary [9], these rate coefficients,  $k_{\text{L,ID}}$ , greatly increase with growing temperature [4].

The experimental data obtained so far [2–4] show values of rate coefficients for  $\text{ArH}_3^+$  reactions which exceed  $k_{\text{L}}$  by typically 10 to 35%, the accuracy of the data being in the range of about  $\pm 10\%$ . In order to stimulate more theoretical work on this subject it is highly desirable to

provide more accurate data than those available so far. We have therefore investigated the reactions of  $\text{ArD}_3^+$  with the neutrals  $\text{C}_3\text{H}_8$  and  $\text{C}_4\text{H}_{10}$ , respectively, with the greatest care, the results for which are reported below. We have chosen these two neutrals for the following reasons: they have practically no permanent dipole ( $\mu(\text{C}_3\text{H}_8) = 0.084$  D and  $\mu(\text{C}_4\text{H}_{10}) \leq 0.5$  D [10]), so that only the ion-induced dipole interaction determines their reactivity with non-polar ions; they also have a high proton affinity, so that they undergo many proton transfer reactions, the rate coefficients of which can be taken as a good reference for their rates of complex formation, as will be shown below; finally, they have large polarizabilities, which means that the location of the maximum centrifugal barriers at thermal collision energies is large ( $R > 6$  Å) compared to the size of the molecules, so that the ion-induced dipole interaction is not distorted by other interactions and one can assume that the measured rate coefficients  $k$  (at least in the case of proton transfer reactions) are very close to, or identical with, the calculated values  $k_{\text{L}}$ .

## 2. Experimental

The apparatus used for the present investigations is a selected ion flow drift tube [11] which has been described in detail in the literature and thus only details specifically pertaining to the present investigation are mentioned here. The reactant ions  $\text{ArH}_3^+$  were produced in the same way as described recently by Praxmarer et al. [4]. Briefly,  $\text{Ar}_2^+$  ions are injected into the drift system where they are allowed to undergo reactions with  $\text{D}_2$ , which finally result in  $\text{D}_3^+$  ions and  $\text{ArD}_3^+$  ions at a ratio of about 100:2; the count rates for  $\text{ArD}_3^+$  are typically 30–50 counts  $\text{s}^{-1}$ . The  $E/N$  (where  $E$  is the electric field strength and  $N$  the helium buffer-gas number density) in the drift section, which was operated at 300 K, was kept in a range from 5 to 12 Td (1 Townsend =  $10^{-17}$  V  $\text{cm}^2$ ). At larger values of  $E/N$  the signal

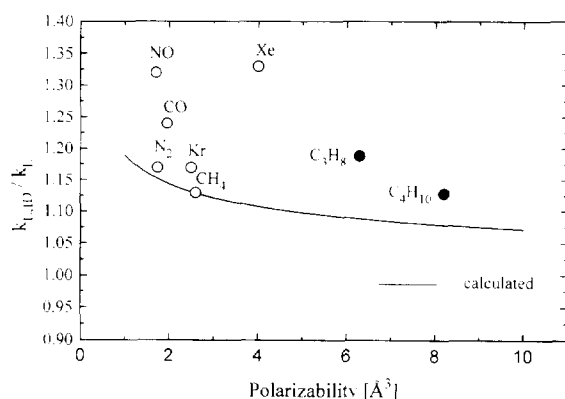


Fig. 1. Calculated ratio  $k_{\text{L,ID}}/k_{\text{L}}$  as a function of the polarizability,  $\alpha$ , for  $\text{ArD}_3^+$  reactions and respective data obtained presently for the reactions of  $\text{ArD}_3^+$  with  $\text{C}_3\text{H}_8$  and  $\text{C}_4\text{H}_{10}$  under near thermal conditions. Also included are recent data from Ref. [4] (O) on reactions of  $\text{ArH}_3^+$  with various neutrals.

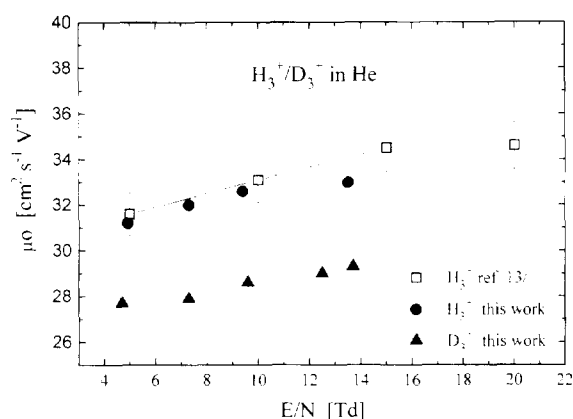


Fig. 2. Reduced mobilities of  $H_3^+$  and  $D_3^+$  ions in helium as dependent on  $E/N$ .

of  $ArD_3^+$  becomes too low to allow for accurate investigations of rate coefficients [4].  $ArD_3^+$  was used as the reactant ion rather than  $ArH_3^+$  because mass 43 appears as a primary and/or secondary ionic product in both of the reactions of  $ArH_3^+$  with  $C_3H_8$  and  $C_4H_{10}$ , while in the case of  $ArD_3^+$  no products appear at  $m/z$  46. In the case of  $ArD_3^+$  reacting with  $C_3H_8$  the proton transfer is solely dissociative, as is the proton transfer from  $D_3^+$  ( $H_3^+$ ) with  $C_3H_8$ , so that no product ion appears at  $m/z$  46.

We obtained the rate coefficients in the same way as described by McFarland et al. [12] from the decline of the primary ion signals when reactant gas was added at a downstream inlet port. The mobilities for  $ArD_3^+$  were obtained from Praxmarer et al. [4], and for the other ions involved, from the compilation of Ellis et al. [13].

However in each case we checked the mobilities, obtaining them as described by McFarland et al. [14]. In all cases our mobilities agreed with those in the literature to within  $\pm 3\%$ . The mobilities of  $D_3^+$  in helium were measured for the first time and are reported below. As both  $D_3^+$  and  $ArD_3^+$  ions were present at the same time, the rate coefficients of the reactions of both ions with the same neutrals were measured simultaneously, so that systematic errors are excluded, for the ratio of  $k_{D_3^+}/k_{ArD_3^+}$ . For comparison, reactions were also measured for  $O_2H^+$ ,  $CO_2H^+$  and  $H_3^+$  with  $C_3H_8$  and with  $C_4H_{10}$ , respectively.

### 3. Results and discussion

Fig. 2 shows the dependence of the mobility of  $D_3^+$  on  $E/N$ , which was needed for the calculation of the rate coefficients of the  $D_3^+$  reactions. For comparison, the mobility of  $H_3^+$  [13] is also included in the figure, as well as data points obtained from the present work.

Table 1 shows the results obtained for the rate coefficients of the reactions of  $O_2H^+$ ,  $CO_2H^+$ ,  $H_3^+$ ,  $D_3^+$  and  $ArD_3^+$  with  $C_3H_8$  and  $C_4H_{10}$ , respectively. The measurements were performed at low  $E/N$  ( $E/N < 12$  Td) and, with the exception of  $ArD_3^+$  reactions, no energy dependence is expected [1]. We denote the rate coefficients as  $k_{300}$  to indicate the temperature of the buffer gas. All values included in Table 1 are averaged values of several measurements. In the case of

Table 1

Thermal rate coefficients obtained for the reactions of various ions with  $C_3H_8$  and  $C_4H_{10}$ , respectively. Also shown are the ratios  $k/k_L$  (measured rate coefficient/Langevin limiting value)

Reactant Ion	$C_3H_8$			$C_4H_{10}$		
	$k$ ( $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ )	$k_L$ ( $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ )	$k/k_L$	$k$ ( $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ )	$k_L$ ( $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ )	$k/k_L$
$O_2H^+$	1.37	1.35	1.01	1.46	1.46	1.00
$CO_2H^+$	1.26	1.24	1.02	1.38	1.33	1.04
$H_3^+$	3.34	3.50	0.97	3.81	3.97	0.96
$D_3^+$	2.44	2.56	0.96	2.77	2.87	0.97
$ArD_3^+$	1.46	1.24	1.18	1.49	1.32	1.13

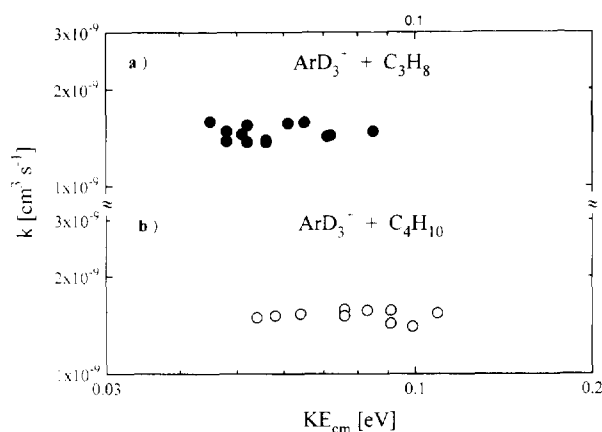


Fig. 3. Reaction rate coefficient,  $k$ , for the reaction  $\text{ArD}_3^+$  with  $\text{C}_3\text{H}_8$  (a) and  $\text{ArD}_3^+$  with  $\text{C}_4\text{H}_{10}$  (b) as a function of the mean relative kinetic energy,  $KE_{\text{cm}}$ , between the reactants.

the reactions of  $\text{ArD}_3^+$ , the individual data points are shown in Fig. 3 as dependent on  $KE_{\text{cm}}$ , the mean relative kinetic energy between the reactants, which was obtained in the usual way [12]. According to the calculations mentioned above [4,8,9], an increase of the rate coefficients for these reactions of about 4% is expected when  $KE_{\text{cm}}$  is raised from 0.04 ( $\sim 300$  K) to 0.1 eV. However, this lies within the scatter of the data for the reactions of  $\text{ArD}_3^+$  with  $\text{C}_3\text{H}_8$  and  $\text{C}_4\text{H}_{10}$ .

Comparison of the measured rate coefficients of the reactions of the non-polar ions with  $\text{C}_3\text{H}_8$  and  $\text{C}_4\text{H}_{10}$  with the corresponding values of  $k_L$  shows agreement to within  $\pm 4\%$  in each case. Therefore, we assume that these reactions indeed proceed at the Langevin limiting rates and that the present measurements have an accuracy of better than  $\pm 10\%$ . The average value for the rate coefficient of the reaction of  $\text{ArD}_3^+$  with  $\text{C}_3\text{H}_8$  is  $k = 1.46 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , which is higher than  $k_L$  ( $k_L = 1.24 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ) by 18%. The value  $k$  for the reaction of  $\text{ArD}_3^+$  with  $\text{C}_4\text{H}_{10}$  is  $k = 1.49 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , which is higher than  $k_L$  ( $k_L = 1.32 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ) by 13%. Both values are included in Fig. 1, together with earlier results on other  $\text{ArH}_3^+$  reactions with non-polar neutrals obtained in this laboratory at 300 K buffer gas temperature. Taking into account an experimental error of  $\pm 10\%$ , both rate coefficients,

$k(\text{C}_3\text{H}_8)$  and  $k(\text{C}_4\text{H}_{10})$ , also lie slightly above the values  $k_{L,\text{ID}}$ , calculated as mentioned above (see Fig. 1) and being  $k = 1.35 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  and  $k = 1.42 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , respectively. The main attempt of this investigation was to obtain data as accurate as possible for  $\text{ArD}_3^+$  reaction rate coefficients, a goal that was achieved satisfactorily. Branching ratios of products, on the other hand, cannot be obtained with comparable accuracy, mainly because of the small count rates of  $\text{ArD}_3^+$ . Therefore we did not make any serious attempts to measure them. We have just learned that Clary [15] has obtained theoretical results on thermal rate coefficients for the reactions of  $\text{ArH}_3^+$  with  $\text{H}_2\text{O}$  ( $k = 2.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ) and with  $\text{NH}_3$  ( $k = 2.4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ ). These values agree extremely well with our experimental values [4], being  $k = 2.5 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  and  $k = 2.6 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  respectively.

We hope that these present data on  $\text{ArD}_3^+$  reactions will stimulate further theoretical work in order to gain more detailed insight into the reactions of polar ions.

### Acknowledgements

This work was supported by Fonds zur Förderung der wissenschaftlichen Forschung by Project P 10014.

## References

- [1] G. Giomousis and D.P. Stevenson, *J. Chem. Phys.* 29 (1958) 294.
- [2] A.B. Rakshit, *Int. J. Mass Spectrom. Ion Processes*, 41 (1982) 185.
- [3] D. Smith, P. Spanel and D. Bedford, *Chem. Phys. Lett.* 191 (1992) 587.
- [4] C. Praxmarer, A. Hansel and W. Lindinger, *J. Chem. Phys.*, 100 (1994) 8884.
- [5] E. Mason and E.E. Mc Daniel, *Transport Properties of Ions in Gases* (John Wiley and Sons, New York, 1988) p. 389.
- [6] M. Bogey, H. Bolvin, C. Bemuyck and J.L. Destomber, *Phys. Rev. Lett.* 58 (1987) 988.
- [7] P. Hobza, R. Zahradnik and D. Smith, *Chem. Phys. Lett.* 208 (1993) 497.
- [8] T. Su and M.T. Bowers, in: *Gas Phase Ion Chemistry*, Vol. 1, ed. M.T. Bowers, (Academic, New York, 1979) p. 84.
- [9] D. Clary, *Ann. Rev. Phys. Chem.* 41 (1990) 61.
- [10] D.R. Lide (editor), *CRC Handbook of Chemistry and Physics* (CRC, Boston, 1990) p. 9.7.
- [11] H. Villinger, J.H. Futrell, A. Saxer, R. Richter and W. Lindinger, *J. Chem. Phys.* 80 (1986) 2543.
- [12] M. McFarland, D.L. Albritton, F.C. Fehsenfeld, E.E. Ferguson and A.L. Schmeltekopf, *J. Chem. Phys.* 59 (1973) 6620.
- [13] H.W. Ellis, R.Y. Pai, E.W. Mc Daniel, E.A. Mason and L.A. Viehland, *Atomic Data and Nucl. Data Tables*, Vol. 17, No. 3 (1976).
- [14] M. Mc Farland, D.L. Albritton, F.C. Fehsenfeld, E.E. Ferguson and A.L. Schmeltekopf, *J. Chem. Phys.* 59 (1973) 6610.
- [15] D. Clary, *Chem. Phys. Lett.*, in press.