Association and charge transfer reactions of $Xe^{\bullet+}$ and $O_2^{\bullet+}$ with acetonitrile

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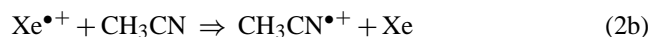[b] Institut für Ionenphysik, Technikerstr. 25, Innsbruck, A-6020, Austria

Abstract

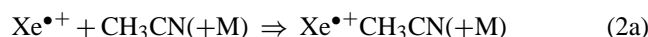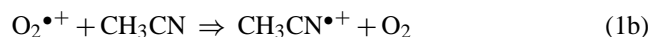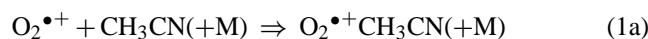The dependences of the effective binary rate coefficient, k_{eff}, for the reactions of $Xe^{\bullet+}$ and $O_2^{\bullet+}$ with CH_3CN were studied by the SIFDT method over in wide ranges of translational energy and buffer gas pressure. The energy dependences indicate a change of the prevailing pathway of the reactions. It is shown that charge transfer changes the three-body association channel while translational energy is increased. The elaborated procedure of the experimental data processing is described. The energy dependences of the parameters characterizing the association process, which have been determined using this procedure, are presented and discussed.
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1. Introduction

Reactions of $O_2^{\bullet+}$ and $Xe^{\bullet+}$ with acetonitrile are good model systems to study the effect of ion/dipole interaction on reaction dynamics. Each of the reactions has two parallel channels—the association and charge transfer:

$$O_2^{\bullet+} + CH_3CN(+M) \Rightarrow O_2^{\bullet+}CH_3CN(+M) \qquad (1a)$$

$$O_2^{\bullet+} + CH_3CN \Rightarrow CH_3CN^{\bullet+} + O_2 \qquad (1b)$$

$$Xe^{\bullet+} + CH_3CN(+M) \Rightarrow Xe^{\bullet+}CH_3CN(+M) \qquad (2a)$$

$$Xe^{\bullet+} + CH_3CN \Rightarrow CH_3CN^{\bullet+} + Xe \qquad (2b)$$

The charge transfer channels ((1b) and (2b)) are slightly endothermic—by 0.13 and 0.07 eV, respectively the (ionization energy of acetonitrile is taken as 12.194 ± 0.005 eV [1]).

The rate constants for the association channels, which have not been measured up to date, are expected to be large at low energy. The rapid association rate may be a result of the formation of "slightly endothermic" complexes in the collisions of the reactants. It is known that the production of such type of intermediates results in a significant enhance of lifetimes of collisional complexes [2,3]. For the above mentioned reactants, the endothermicity of the charge transfer is small enough and the production of "long-lived" intermediates may be expected. A significant anisotropy of the interaction between the reacting particles may also result in an increase of the decay time of the complexes [2].

It is known that a relation between the rates of the decay and stabilization defines the pressure range, where the dependence of the association rate becomes non-linear. When the pressure dependence is non-linear, it is possible to determine the values of the parameters, which characterize the association process. For the reactions studied in the present work the dependences are non-linear at low energy.

The ratio between the association and charge transfer channels for the reactions should depend on energy. At low energy, the association is fast while the charge transfer reaction should be slow due to its endothermicity. At high enough translational energy, the association channel should become

slow (due to a decrease of the complex lifetime) while the endoergic channel is expected to be prevailing.

The goals of the present work are:

(1) To study the change of the prevailing mechanism of the reactions from ((1a) and (2a)) to ((1b) and (2b)) as a function of translational energy increase.
(2) To study the energy dependences of the parameters, which characterize the association process.

2. Experimental

All experiments were carried out using the Innsbruck SIFDT machine as described elsewhere [4,5] in the pressure range of the buffer gas (He) 0.12–0.7 Torr at room temperature ($T = 293$ K). Translational energy (E_{cm}) was varied in the range of 0.042–4 eV. Primary ions ($Xe^{\bullet+}$ or $O_2^{\bullet+}$) were produced in a hollow cathode discharge, mass selected by the first quadrupole and injected into the drift tube. The measurement of the ion current of the $^{129}Xe^{\bullet+}$ isotope was used to evaluate the total intensity of the primary ions in the experiments with Xe. The length of the reaction region (the distance between the inlet port of acetonitrile and the nose cone, which samples ions for a mass analysis by the second quadrupole) was 62.5 cm.

A fraction of primary ions was produced in the ion source in excited states. The presence of excited ions may play an important role and many affect the behavior of the kinetic dependencies (ion current versus flow of acetonitrile). A procedure using COS as a monitor gas [6] was applied to estimate a fraction of $Xe^{\bullet+}$ ions in the excited ($^2P_{1/2}$) state. The estimation is based on a difference in the rate constants of reaction of $Xe^+ + COS$ for the $^2P_{3/2}$ and $^2P_{1/2}$ ionic states. The "weights" of the fractions of the states were determined using a "two exponential decay" fitting function approximating kinetic dependences. A fraction of the excited ions depended on the discharge conditions (pressure and current) and could be varied within the range 5–15%.

While studying the reaction $O_2^{\bullet+} + CH_3CN$, O_2 (>0.01% of the buffer gas flow) was admixed upstream of the inlet port of the neutral reactant to quench any possible excitation of $O_2^{\bullet+}$.

3. Results and discussion

The values of the effective binary rate coefficient k_{eff} have been determined from the plots of the ion current logarithm (for the $O_2^{\bullet+}$ and $Xe^{\bullet+}$ ions) versus the flow of acetonitrile. Figs. 1 and 2 show the dependences of k_{eff} on the relative translational energy E_{cm} (in the center of mass system) of the reactants.

It follows from the figures that the curves are very similar for the studied systems. The difference in a fraction of the excited $Xe^{\bullet+}$ ions does not practically affect the behavior of the curves. Nevertheless the operation mode of the discharge
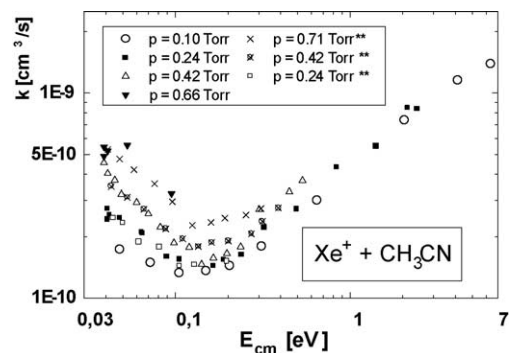

Fig. 1. Energy dependences of k_{eff} for the $Xe^{\bullet+} + CH_3CN$ system at various pressures. Asterisks indicate data, when the fraction of the excited $Xe^{\bullet+}$ ions is 5%. For the rest of the curves the fraction is 15%.

was selected to provide the lowest level of the fraction of the excited ions.

At $E_{cm} < 0.1$ eV, the dependences of k_{eff} significantly diverge at various pressures of the buffer gas and show a decrease with energy. The curves become independent on pressure at $E_{cm} > 0.7$ eV, and they increase with E_{cm}. The behavior of the curves demonstrates a significant contribution of the association channel to the reaction rate at low energy, while the charge transfer becomes prevailing only at high enough energy.

A detailed information on the association processes may be obtained from the pressure dependences of the rate constants. Sets of such dependencies ($E_{cm} \leq 100$ meV) are shown in Figs. 3 and 4. At $E_{cm} > 100$ meV, the curves are practically linear and have not been treated.

For the treatment of the experimental curves k_{eff} is presented as:

$$k_{eff} = k_0 + k_a = k_0 + \frac{k_C(k_S/K_d)M}{1 + (k_S/K_d)M}, \qquad (3)$$

i.e. by the sum of a charge transfer rate constant k_0 and k_a (given by an expression for the binary rate coefficient of the association process, which is dependent on the buffer gas concentration M). k_a is presented as a function of two parameters, k_C and the ratio k_S/K_d. k_C is the rate constant for
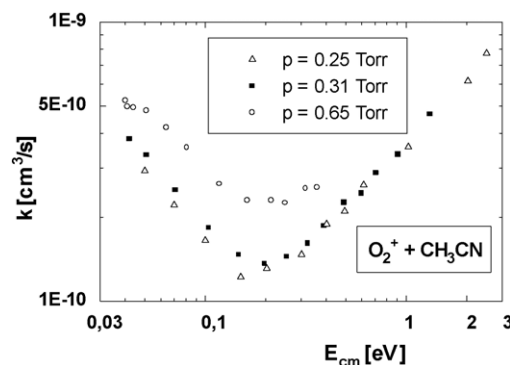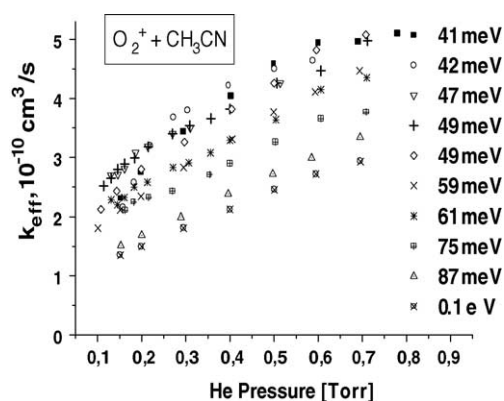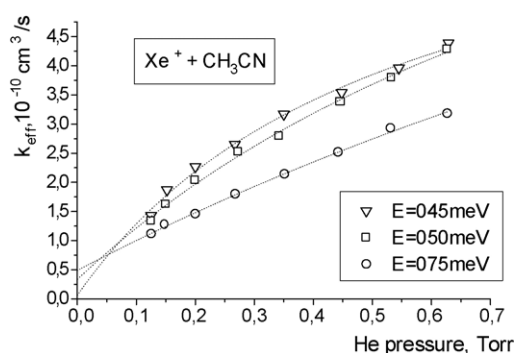

Fig. 2. Energy dependences of k_{eff} at different pressures for the $O_2^{\bullet+} + CH_3CN$ system.

Fig. 3. Pressure dependence of k_{eff} for the $O_2^{\bullet+} + CH_3CN$ system.

Fig. 4. Pressure dependence of k_{eff} for the $Xe^{\bullet+} + CH_3CN$ system.

the formation of a complex, which can either undergo a reverse decay with a characteristic time $1/K_d$ or can be stabilized by collision with He. k_S is the rate constant of the corresponding stabilization process. While expression (3) is based on a simplified Lindeman–Hinshelwood model, it allows the presentation of the parameters in a simpler way than the sophisticated models based on phase space theory [7,8].

The main advantage of the presentation of the association rate coefficient by (3) is the following. It is not necessary to assume that k_C is strictly equal to the collision rate con-

stant k_{C0}. The comparison of k_C and k_{C0} can give a factor $P_C = k_C/k_{C0}$, whose value may indicate, that not all the collisional complexes make equal contributions to the association rate. The approach can be applied only for non-linear pressure dependences, when the transition from the third to the second order of the association reaction takes place. In the course of the treatment an attempt has been made to determine simultaneously all the parameters (k_C, k_S/K_d and k_0) from each of the experimental curves $k_{eff}(P)$ presented in Figs. 3 and 4. The fitting function is given by expression (3). The number of parameters is rather large to expect a good accuracy of their estimation and the results may be used only for preliminary analysis. The results of the treatment are shown in Tables 1 and 2.

It follows from Tables 1 and 2 that k_C is smaller than the collisional rate constant k_{C0} and increases with energy. The value of k_{C0} can be evaluated using the ADO model, which takes into account the interactions of permanent and induced dipoles with ions [9,10]. An estimated value of k_{C0} (at $E_{cm} \approx 0.04$ eV) is about 4×10^{-9} cm^3/s for the $O_2^{\bullet+} + CH_3CN$ collisions. Thus, the probability factor $P_C = k_C/k_{C0}$ is significantly less than unity. The calculated value of k_{C0} for the collisions of $Xe^{\bullet+}$ with CH_3CN does not differ much from the previous estimation (being about 3×10^{-9} cm^3/s) and the probability factor P_C is also small.

The decrease of the association rate with energy is a result of the decrease of the k_S/K_d parameter. It is reasonable to assume that k_S is not dependent on energy. When the ions are drifting in the electric field, the translational energy (in the center of mass system) of the stabilizing collisions ($O_2^{\bullet+}CH_3CN + He$ and $Xe^{\bullet+}CH_3CN + He$) is significantly less than that for the collisions of the respective precursor ions with acetonitrile. The reduced mass for collisions with He is significantly less than for acetonitrile. The energy of the stabilizing collisions is estimated close to thermal energy, which is defined by the bath gas temperature. It is valid when the energy of the collisions of the precursor ions with acetonitrile is less than 0.1 eV.

Thus, the energy dependence of the k_S/K_d parameter should correspond to a behavior of the complex lifetime. It

Table 1
Values of parameters involved in expression (3) for $O_2^{\bullet+} + CH_3CN$ (+M) reaction at various translational energies

E_{cm} (eV)	k_C (10^{-10} cm^3/s)	k_S/K_d		k_0 (10^{-10} cm^3/s)
		Torr^{-1}	10^{-16} cm^3	
0.041	7.4 ± 0.24[a]	3.0 ± 0.7[a]	0.86 ± 0.2[a]	0.05 ± 0.36[a]
0.042	6.8 ± 0.5[a]	4.0 ± 0.7[a]	$1,14 \pm 0.2$[a]	0[b]
0.047	5.7 ± 1.3[a]	1.5 ± 0.8[a]	0.43 ± 0.23[a]	1.7 ± 0.3[a]
0.049	9.2 ± 2.5[a]	0.65 ± 0.3[a]	0.19 ± 0.09[a]	2.0 ± 0.2[a]
0.049	12 ± 3.0[a]	0.63 ± 0.2[a]	0.185 ± 0.06[a]	1.3 ± 0.4[a]
0.058	13.1 ± 1.4[a]	0.47 ± 0.08[a]	0.13 ± 0.02[a]	1.2 ± 0.4[a]
0.061	19 ± 4[a]	0.24 ± 0.05[a]	0.069 ± 0.015[a]	1.6[b]
0.075	23[b]	0.18 ± 0.01[a]	0.052 ± 0.003[a]	1.4 ± 0.1[a]
0.087	21 ± 5[a]	0.19 ± 0.04[a]	0.054 ± 0.012[a]	0.93 ± 0.3[a]
0.101	28[b]	0.11 ± 0.01[a]	$0,03 \pm 0.003$[a]	0.87 ± 0.4[a]

[a] The error limits correspond to the fitting procedure only.
[b] The indicated value is set fixed in a fitting procedure.

Table 2
Values of parameters involved in expression (3) for $Xe^{+\bullet} + CH_3CN$ (+M) reaction at various translational energies

E_{cm} (eV)	k_C (10^{-10} cm³/s)	k_S/K_d		k_0 (10^{-10} cm³/s)
		Torr^{-1}	10^{-16} cm³	
0.045	7.9 ± 0.8[a]	1.84 ± 0.7[a]	0.53 ± 0.02[a]	0.06 ± 0.36[a]
0.050	11.1 ± 2.4[a]	0.86[a] ± 0.34	0.25 ± 0.01[a]	0.33 ± 0.2[a]
0.075	15 ± 5.8[a]	0.35[a] ± 0.18	0.1 ± 0.005	0.49 ± 0.08[a]

[a] The error limits correspond to the fitting procedure only.

is not possible to determine k_S in the present experiment directly. So the subsequent estimation of the lifetime $\tau = 1/K_d$ requires a "guess" for the magnitude of k_S. For the present estimation the probability is taken to amount to Cu—30% per collision. As the rate constant for collisions of the ion complexes with helium is about 10^{-9} cm³/s, the "guess" value for k_S will be taken equal to 0.3×10^{-9} cm³/s. The values of k_S/K_d are presented in Tables 1 and 2 in Torr^{-1} and 10^{-16} cm³ (reciprocal concentration) units. The lifetimes $\tau = 1/K_d$ at various energy may be evaluated taking into account that, when $k_S/K_d = 1$ Torr^{-1}, $\tau \approx 0.84 10^{-7}$ s. The reason for high lifetime values will be discussed below. It should be noted that a semi-empirical calculation (HyperChem Program, PM3) gives a binding energy of about 40 kcal/mol for the $O_2^{\bullet+}CH_3CN$ complex.

As has been mentioned, the reliability of the estimation of the parameters (k_0, k_C and k_S/K_d) is not good because three parameters are determined simultaneously from one experimental curve by the fitting procedure. The values of k_0, which have been determined in the fitting procedure, may characterize rather an optimal position for the intersection of the fit curve with the Y-axis rather than the real value of k_0. The reliability of the estimations may be improved, if the number of variable parameters is reduced.

The accuracy of the determination of k_0 is critically dependent on the accuracy of the experimental points at low pressure (see Figs. 3 and 4). It is known that at buffer gas pressure below 0.2 Torr the accuracy of the measurements of rate constants by the drift tube method is not good. Usually such measurements give overestimated values [11]. The reason for this is an effect of the admission of a reactant gas on the "effective ion mobility" in the gas mixture, which may result in an increase of the reaction time. So, the data indicated in the last column (k_0) in Tables 1 and 2 may refer to the best-fit values rather than to the rate constant of the charge transfer reaction.

The reliability of the estimations of the parameters may be improved if k_0 is determined by an independent way. One way is an estimation of rate constant at very low pressure, when the contribution of the association channel is negligible. A preliminary estimation was made by one of the authors by using the ICR technique. Another estimation was based on an analysis of kinetic dependence for the $CH_3CN^{\bullet+}$ product. The measurements were made by the flowing afterglow technique (FA) in He. It has been found, that the values are about 7 and 4×10^{-11} cm³/s (for ICR and FA respectively) at room temperature.

In the present work the independent evaluations of k_0 have been made from kinetic dependences of $CH_3CN^{\bullet+}$ production. The ratio of the ion currents (product over precursor) for the $O_2^{\bullet+} + CH_3CN$ system is given by the expression:

$$\frac{i_{41}}{i_{32}} = \frac{f_{41/32}k_0}{(k_p - k_{eff})} \left\{ 1 - \exp[-(k_p - k_{eff})[A]t] \right\}. \quad (4)$$

The subscripts for i are matching the m/z values of the ion currents. $f_{41/32}$ is a factor, which takes into account a detection efficiency of the ions. It is related with the "discrimination effects", which arise, when ions are sampled and detected by the quadrupole mass analyzer. $[A]$ is the concentration of acetonitrile and t is the reaction time. k_p is the rate constant of the loss of the secondary molecular ions of acetonitrile in the reaction $CH_3CN^{\bullet+} + CH_3CN \rightarrow CH_3CNH^+ + CH_2CN^\bullet$. The value of $k_p = 2 \ 10^{-9}$ cm³/s was taken from [12,13]. k_p is significantly higher than k_{eff}, so the i_{41}/i_{32} ratio should reach its steady level at a moderately small flow of acetonitrile. The values of the steady level of (4) (being equal to $f_{41/32}k_0/(k_p - k_{eff})$) were determined from the kinetic dependences of the i_{41}/i_{32} ratio on the flow of acetonitrile at various pressures and energies. So, k_0 could be easily calculated. The factor $f_{41/32}$ was estimated about 1.1. The values of k_{eff} were determined from the "exponential decay curves" of the primary ions, which were measured in parallel. The results of estimations of k_0 at various pressures are shown in Fig. 5.

When analyzing the results determined from the kinetic dependences of the secondary ions it is important to be sure that the "scale of the reaction time" for the primary and sec-
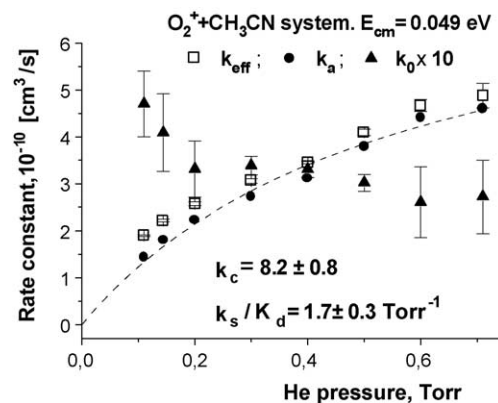

Fig. 5. Pressure dependences of contributions of charge transfer (k_0) and association (k_a) rate constants to k_{eff} at translational energy 0.049 eV. The dashed line is the best-fit curve for k_a. k_C units are 10^{-10} cm³ s^{-1}.
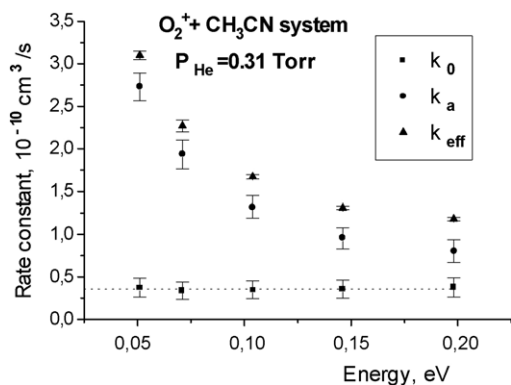
Fig. 6. Energy dependences of the effective binary rate coefficient k_{eff} and the contribution of the association rate constant k_a at a pressure of the buffer gas 0.31 Torr for the $O_2^{\bullet} + CH_3CN$ system.

Fig. 7. Dependence of k_C on translational energy for the $O_2^{\bullet} + CH_3CN$ system.

ondary ions is the same. When the method of evaluations of k_0 from the steady level of the ratio is used, the result does not depend on a characteristic time to reach the level. A difference in the rate of the loss between the primary and secondary ions due to their diffusion may also affect on the accuracy of the estimation. A detailed analysis shows that the difference does not play any role at pressure above 0.3 Torr. For the studied range below 0.3 Torr a contribution of the effect does not exceed the error margins, which correspond to the experimental points scatter.

It has been mentioned that the measurements of the rate constants at pressure below 0.2 Torr give overestimated values. If the points below 0.2 Torr are not taken into account it may be concluded, that the rate constant of the charge transfer channel does practically not depend on the he pressure, as it follows from Fig. 5. The value of k_0 averaged for various energies (see Fig. 6) equals to 0.37×10^{-11} cm^3/s.

The dashed curve in Fig. 5 presents the fitting function for the effective binary rate constant of the association channel ($k_a = k_{eff} - k_0$), which is given by the second term of expression (3). The optimal values of two parameters (k_C and k_S/K_D) are given in the figure. They significantly differ from those indicated in the matching line in Table 1 (corresponding to the results of the fits, when three parameters have been determined from the dependence $k_{eff} = f(P)$).

It should be noted that the reliability of the measurements of rate constants at pressure above 0.6 Torr might be not high. The reason is an effect of scattering of ions, when they are sampled into the high vacuum section of the apparatus. The effect brings to a low intensity of detected signals and results in a large scatter of experimental points. Then it is better not to take such experimental points into account. While an agreement between the experimental point of k_a and "the best-fit curve" at the largest pressure of He is good for the measurements shown in Fig. 5, it is not so for some of the similar measurements at other energies.

Fig. 6 shows the dependence on energy of the contributions of k_a and k_0 to k_{eff}. The contribution of k_0 has been determined
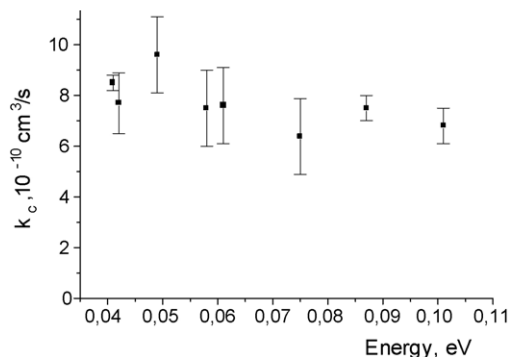
from the i_{41}/i_{32} ratio for the extended energy range (up to 0.2 eV).

The approach (demonstrated by Fig. 5) has been applied to the treatment of experimental data at energy below 0.1 eV (to correct the results given in Table 1). The corrected values of the parameters characterizing the association process, which have been determined from the pressure dependences of k_a at different energies, are presented in Figs. 7 and 8.

It should be noted that the effective rate constant of the association channel is rather large at low translational energy. The low-pressure limit of the three-body association rate constant (in cm^6 s^{-1} units) may be expressed as

$$k_{a0} = k_C \left(\frac{k_S}{K_d} \right).$$

The evaluation of k_{a0} for the lowest energy (about 0.042 eV) gives

$$k_{a0} \approx (5 \pm 2.1) \times 10^{-26} \text{ cm}^6 \text{ s}^{-1}.$$

It may be shown that the evaluation of the three-body rate constant by the expression $k_{a0} = (k_{eff} - k_0)[M]$ gives noticeably overestimated values in the studied pressure range at low energy.

The large values of rate constants for the studied systems are in agreement with the concept, which predicts long lifetimes, when a slightly endothermic charge transfer may take
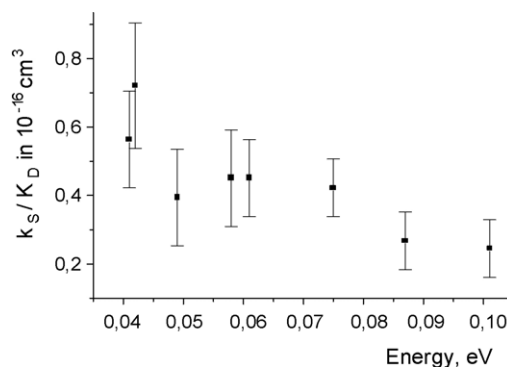

Fig. 8. Dependence of k_S/k_d ratio on translational energy for the $O_2^{\bullet} + CH_3CN$ system.

place [2,3]. Anisotropy of interaction between the colliding particles may also result in long lifetimes of the complex [3]. Acetonitrile is a very polar molecule, whose dipole momentum is about 4 Debye units.

The difference in k_C and the rate constant of collisions is surprisingly large (by a factor about 5). A physical meaning of the result may be understood if one assumes, that the formation of a complex, whose lifetime is long (corresponding to the determined value of k_S/K_d), does not occur in each collision. About 80% of the trajectories result in the formation of the complexes, whose lifetime is small so, that the contribution of such collisions is of no importance for the rate constant. For the studied system it is so, if the "partial" three-body rate constant for those 80% of collisions does not exceed several 10^{-28} cm^6 s^{-1} units.

The explanation given above is simplified but seems rather explicit. One cannot exclude that the formation of the "long lived" fraction of collision complexes may occur due to a non-adiabatic transition to a term with close energy. In any case a possible production of a variety of complexes, whose lifetimes significantly differ, should be taken into account in sophisticated models, which are more complicated than the simple model used in the present work for the treatment and interpretation of results.

It follows from Fig. 6 that k_0 does not practically depend on translational energy. The behavior of the dependence is not typical for rate constants of endothermic reactions. It should be noted that a fraction of the secondary ions with $m/z = 41$ may be produced in an exothermic reaction of the primary ions with acetonitrile.[1] As k_0 has been determined from the production of the secondary ions (with $m/z = 41$) its estimate may involve a contribution of the exothermic process. So the interpretation of the energy dependence is not easy.

4. Conclusions

It has been found that the change of the prevailing channel of reactions $Xe^{\bullet+} + CH_3CN$ and $O_2^{\bullet+} + CH_3CN$ takes place at translational energy about several hundreds meV in the He pressure range 0.2–0.6 Torr. The charge transfer channel is prevailing at high energy.

The rate constant for the production of $CH_3CN^{\bullet+}$ ions does not practically depend on the buffer gas pressure at least at low energy and in the pressure range 0.2–0.6 Torr.

A large rate of the association process at low energy is a result of a long lifetime of collisional complexes, which is estimated about 10^{-7} s. The result is in agreement with the model predicting long lifetimes of collision complexes, in which slightly endothermic charge transfer may take place.

A treatment procedure of experimental dependences based on a simple model of association processes has been elaborated. It has been shown that only 20% of collisions make the main contribution to the association rate in the studied pressure range at low energy.

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[1] Quantum chemistry calculations indicate that the isomeric ion whose structure is $^{\bullet}CH_2CNH^+$ has lower energy than the ion with the structure of the neutral precursor acetonitrile molecule. Recently the authors have obtained experimental and theoretical evidences of the isomerisation process, which may be the subject of a separate publication.