

Kinetics of secondary ion complexes in $O_2^{\bullet+}CH_3CN$ and $Xe^{\bullet+}CH_3CN$ systems

Formation of nonprotonated ion complexes of acetonitrile

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Received 6 December 2004; accepted 10 December 2004

Available online 2 March 2005

Abstract

A detailed kinetic study for the production of secondary and ternary ions in O_2^+ (Xe^+)– CH_3CN systems was made by applying the SIFDT techniques. “Nonprotonated complexes” (cation radical dimers or higher aggregates) of acetonitrile were present in the mass spectra of product ions. The formation of nonprotonated dimers of acetonitrile ions is ascribed to switching reactions of the ion complexes $[O_2^{\bullet+}CH_3CN]$ and $[Xe^{\bullet+}CH_3CN]$ with acetonitrile. Mathematical procedures for the treatment of kinetic dependences, in which the rate constants of the studied reactions have been determined, are described. Energy and pressure dependences of the rate constants are presented and discussed. © 2004 Elsevier B.V. All rights reserved.

Keywords: Ion/molecule reaction; Clusters; Cation radical dimers; Switching reactions; Fitting

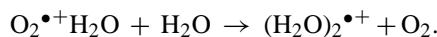
1. Introduction

Reactions of ions with acetonitrile are a good model to study some of the specific features of reactivity in ion/dipole collisional complexes. Due to the large dipole moment of CH_3CN (about 4 Debye units), a strong alignment of particles in the complex is expected. While slightly endoergic charge transfer reactions $O_2^+ + CH_3CN$ and $Xe^+ + CH_3CN$ appear to be very slow, the association channel is very efficient, when the buffer gas pressure exceeds 0.2 Torr and the translational energy is less than 300 meV [1].

The subject of the present work concerns the reaction kinetics of the secondary and ternary ions produced in the $O_2^+ + CH_3CN$ and $Xe^+ + CH_3CN$ systems. Preliminary experiments, which have been made by the Moscow group using the flow technique apparatus, have shown that one of

the products of the transformations is an ion with $m/z = 82$. It may be ascribed to the nonprotonated acetonitrile ionic dimer (radical). Moreover, the ions with $m/z = 123$ (nonprotonated cation radical trimer) have been also observed in mass spectra.

The formation of odd electron water dimers (and clusters) is a very interesting phenomenon, which is known since the end of the 1960s. It cannot occur directly in a three-body association process. The $[H_2OH_2O^{\bullet+}]$ intermediate, which is formed in collisions, should undergo a fast reactive decay producing the protonated product. The mechanism of formation of nonprotonated water ions is known and described in the literature [2,3]. These “nonprotonated dimers” are produced in switching reactions of some stable precursor ion complexes. For example, in the $O_2^{\bullet+} - H_2O$ system the dimer is produced from the $O_2^{\bullet+}H_2O$ precursor (the product of the initial association stage) in the reaction:



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Thermochemical properties and the reactivity of the water dimer radical cation have been the subject of detailed studies [4,5]. The key role of the switching reactions in the production of cation radical dimers was found for a number of other reaction systems as well [6].

Up to date, there are no experimental data on the binding energy of the $O_2^{\bullet+}CH_3CN$ cluster. Our estimation, which is based on semi-empirical calculations, gives a value of about 40 kcal/mol. It may be shown that along with the formation of the nonprotonated dimer in the $O_2^{\bullet+}CH_3CN + CH_3CN$ switching reaction a parallel channel, in which protonated acetonitrile is produced, is thermochemically allowed, being exothermic about 20 kcal/mol. The estimation takes into account the following thermochemical reference data [7,8]: the C–H bond energy in CH_3CN (92 kcal/mol), the proton affinity of acetonitrile (186.2 kcal/mol), ionization potentials of O_2 and H (12.07 and 13.6 eV, respectively). The binding energy of the $O_2^{\bullet+}CH_3CN$ is taken equal to 40 kcal/mol.

Due to the exothermicity of the CH_3CNH^+ production in the parallel channel, the stable cation radical dimer can be formed only when the energy, which is removed by the O_2 product particle, exceeds the above-mentioned value (20 kcal/mol). Otherwise, the excitation energy of the $[CH_3CN]_2^{\bullet+}$ product exceeds the threshold of its “reactive decay”, in which the CH_3CNH^+ product is formed. The decay takes place if the excessive excitation is not quenched. An experimental study of the reaction kinetics may provide important information on the reactions mechanisms of odd electron clusters, which are not simple.

The goal of the present work is to study the kinetics of transformations of $O_2^{\bullet+}CH_3CN$ and $Xe^{\bullet+}CH_3CN$ complexes, to elaborate procedures of the treatment of kinetic dependences, and to obtain quantitative data on the rate constants of the reactions.

2. Experimental

The experiments were carried out using the Innsbruck SIFDT machine as described elsewhere [9,10]. Experimental conditions were: buffer gas, He; pressure, 0.12–0.7 Torr; temperature, 297 K; translational energy, 0.042 ± 0.4 eV. The primary ions $Xe^{\bullet+}$ and $O_2^{\bullet+}$ were produced in a hollow cathode discharge. The COS monitor gas method [11] was used to estimate the fraction of $Xe^{\bullet+}$ in its $^2P_{1/2}$ state. The fraction of the excited state could be controlled by the conditions of the discharge and was minimized. While studying reactions in the $O_2^{\bullet+} + CH_3CN$ system, a small flux of O_2 (>0.01% of the bath gas flow) was added to quench any initial vibrational and electronic excitation of the $O_2^{\bullet+}$ primary ions.

For each of the systems, the kinetic dependences of the mass spectra (ion currents versus the flow of acetonitrile) were studied at various pressures of the buffer gas and translational energies. The rate constants have been determined from the treatment procedures, which will be described later.

Experiments using the Moscow (IEPCP) FA apparatus were made at 1 Torr buffer gas pressure and $T = 290$ K. The contact time (varied by the length of the region of reaction) and the acetonitrile flow rate were variable parameters for kinetic dependences.

3. Results and discussion

Examples of the kinetic dependences of the mass spectra are shown in Fig. 1a and b. They demonstrate that an efficient production of “nonprotonated” clusters of acetonitrile (dimer and trimer cation radicals) takes place. The analysis of the kinetic dependences leads to the scheme for ionic transformations as shown in Fig. 2.

A special procedure for the data treatment has been elaborated to obtain quantitative information on the reactions of the $X^{\bullet+}CH_3CN$ ($X = O_2, Xe$) and $(CH_3CN)_2^{\bullet+}$ species. The procedure is based on the following approach. Analytic expressions for the kinetic dependences of the ionic concentrations, which are proportional to the measured ion currents, are obtained from the solution of the system of the ordinary differential equations, corresponding to the kinetic scheme. Similar expressions for the ion currents, which involve some proportionality factors, are used as fitting functions in the subsequent fitting procedures, in which the rate constants are determined. The concentrations of the secondary and ternary

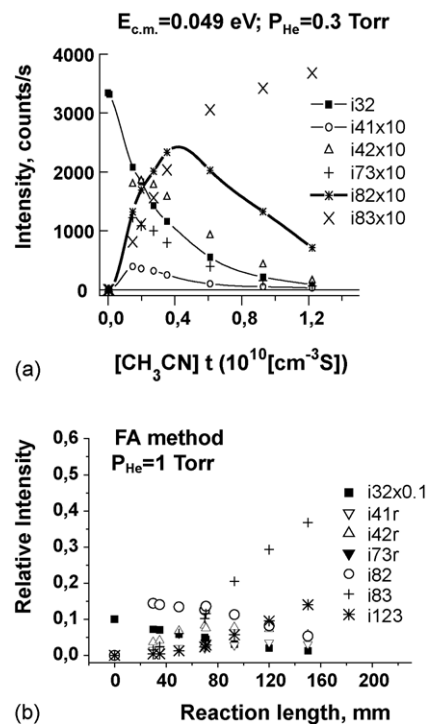


Fig. 1. (a) An example of the dependence of a mass spectrum on the $[CH_3CN]_t$ kinetic variable obtained in the SIFDT study of the $O_2^{\bullet+} + CH_3CN$ system. (b) An example of the dependence of a mass spectrum on the length of the reaction range for the $O_2^{\bullet+} + CH_3CN$ system (FA method).

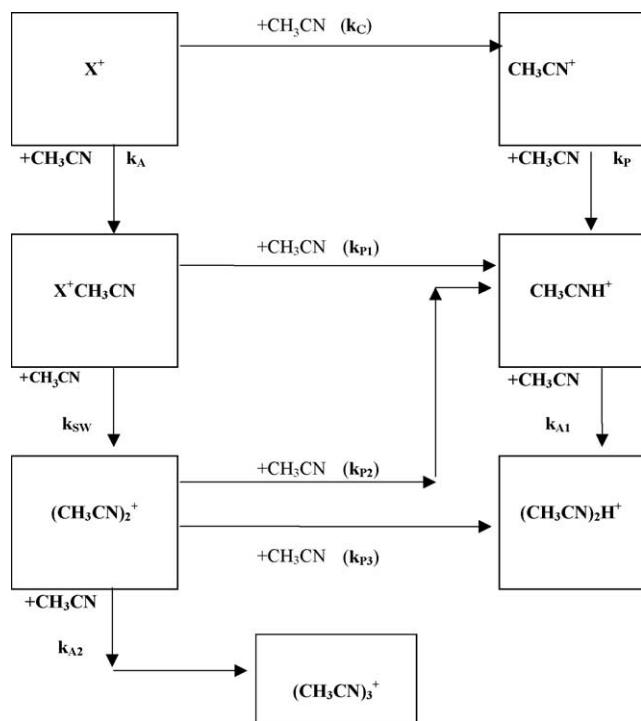


Fig. 2. The scheme of ion transformations in $O_2^{\bullet+}$ ($Xe^{\bullet+}$) + CH_3CN systems.

ions are given by:

$$[O_2^{\bullet+}CH_3CN] = [O_2^{\bullet+}]_0 \left[\frac{k_A}{k_E - k_{eff}} \right] [\exp(-k_{eff}nt) - \exp(-k_Ent)], \quad (1)$$

$$[(CH_3CN)_2^{\bullet+}] = \frac{[O_2^{\bullet+}]_0 k_A k_{SW}}{(k_E - k_{eff})(k_F - k_{eff})(k_F - k_E)} \times \{(k_F - k_E)[\exp(-k_{eff}nt) - \exp(-k_Ent)] - (k_E - k_{eff}) \times [\exp(-k_Ent) - \exp(-k_Fnt)]\}. \quad (2)$$

$[O_2^{\bullet+}]_0$ is the initial concentration of the primary ions, n is the concentration of acetonitrile. $k_{eff} = k_C + k_A$ is the effective binary rate coefficient determined from the exponential decay plot of the primary ion. Note that the main contribution to k_{eff} at low energy provides the rate constant of the association, while the rate constant of the slightly endoergic charge transfer k_C is small, so k_{eff} is pressure dependent [1]. $k_E = k_{SW} + k_{P1}$ is the rate constant for the total loss of the $O_2^{\bullet+}CH_3CN$ ion in parallel reactions. The loss of the “non-protonated dimers” may take place in three channels, so the rate constant is $k_F = k_{A2} + k_{P2} + k_{P3}$ (see Fig. 2).

The current of the secondary cluster ion may be expressed by:

$$i_{73} = A_{73} F_{S73} = A_{73} \left[\frac{1}{k_E - k_{eff}} \right] [\exp(-k_{eff}nt) - \exp(-k_Ent)]. \quad (3)$$

The current is presented as a product of the “scaling” factor A_{73} and the “shape function” $F_{S73}(nt) = [1/(k_E - k_{eff})] [\exp(-k_{eff}nt) - \exp(-k_Ent)]$. A_{73} depends on the initial current of the primary ion (at $n=0$), the detection efficiency of the $O_2^{\bullet+}CH_3CN$ ion and k_A :

$$A_{73} = i_{32}(0) f_{73/32} k_A. \quad (4)$$

The factor $f_{73/32}$ takes into account the discriminations produced by the sampling system and the quadrupole mass analyzer. k_{eff} is determined prior to the treatment of the data for secondary ions from the exponential decay curve of the primary ion. So, while treating the dependences of the secondary ions only two variable parameters, i.e., k_E and A_{73} are determined in the fitting procedure (using (3) as a fitting function).

The expression for the current of the $(CH_3CN)_2^{\bullet+}$ ion may be derived in a similar way. In this case, the discrimination effect is also included in the “scaling” factor $A_{82} = i_{32}(0) k_A k_{SW} f_{82/32}$. The “shape function” F_{S82} is taken from expression (2). Fig. 3a and b illustrate two examples for an application of the procedure.

Note that branching ratios of the channels may be evaluated directly only when additional information on the discrimination factors is available.

The dynamic processes (ion transport in the drift tube) may affect the accuracy of the estimations. Here, they are

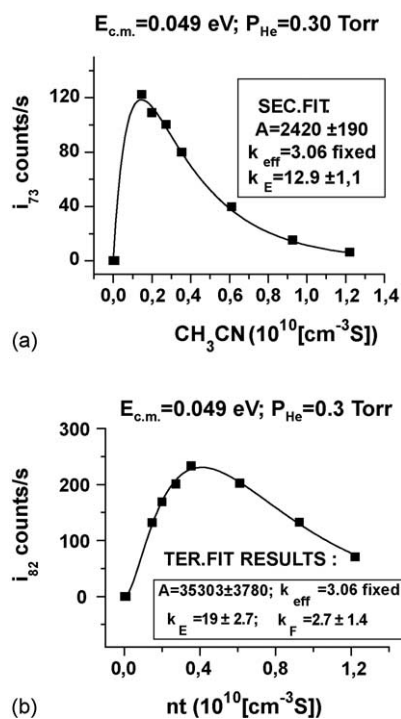


Fig. 3. (a) An estimation of k_E from the experimental dependence of the current of the secondary $O_2^{\bullet+}CH_3CN$ ion. Expression (3) is used as the fitting function (SEC.FIT). Solid line is the best-fit curve. k_E is given in $10^{-10} \text{ cm}^3/\text{s}$ units. (b) An estimation of k_E and k_F from the experimental dependence of i_{82} ($(CH_3CN)_2^{\bullet+}$ ternary ion) using the fitting function (derived from (2), TER.FIT). Solid line is the best-fit curve. k_E and k_F are given in $10^{-10} \text{ cm}^3/\text{s}$ units.

not taken into account in the expressions given above. First of all, it is important to be sure that the scale of the reaction time t for the primary and the secondary ions is the same. The reason to assume this is due to the close values of mobility for different ions in helium. A possible relative correction $\Delta t/t$ in the arguments of exponents in (3) is significantly smaller than the error margins of the fitting procedure.

Another possible effect of the transport processes is related with a difference in the loss rates for different ions due to transversal diffusion. It can be shown that the effect plays no role, provided these rates are equal. The effect of the difference in transport properties of ions on the accuracy of the rate constant estimation is considered in Appendix A.

The treatment procedure illustrated by Fig. 3a and b has been applied to sets of kinetic dependences of mass spectra at various experimental conditions. Dependences of k_E and k_F on pressure of the buffer gas are shown in Fig. 4a. The values of k_E obtained from fits of the kinetic curves for secondary ions (SEC.FIT) and ternary ions (TER.FIT) are different. Yet, the agreement between the values may be considered as satisfactory, taking into account that for the ternary ions three parameters have been determined from each of the curves. The error bars indicated in the figure correspond to errors of the fitting procedure only. The experimental points at pressure below 0.2 Torr and above 0.6 Torr are not reliable for the SIFDT apparatus. For the range of 0.2–0.6 Torr, k_E is not dependent on pressure. The averaged k_E value determined from the secondary ion kinetics (SEC.FIT):

$$k_E = 15 \pm 3 \times 10^{-10} \text{ cm}^3/\text{s} \quad (5)$$

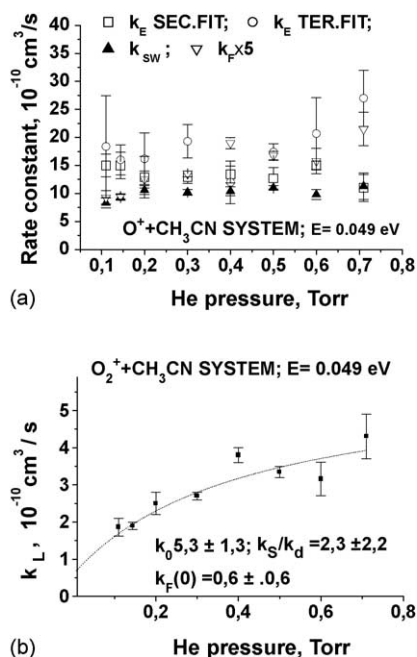


Fig. 4. (a) Pressure dependences of rate constants. k_E values are determined from kinetics of the secondary (SEC.FIT) and ternary ions (TER.FIT). (b) Results of the fitting of the pressure dependence of k_F using (7). The dashed line is the best-fit curve. Units of k_0 and $k_F(0)$ are $10^{-10} \text{ cm}^3/\text{s}$; units of k_s/k_d are Torr^{-1} .

is in agreement with the TER.FIT estimations within the error margins.

An estimation of the rate constant for the switching channel was made from the ratio of ion currents i_{82}/i_{73} . At low values of nt when the arguments of all exponential functions— $(k_j nt)$ are less than unity the ratio may be presented as $i_{82}/i_{73} \approx 1/2 f_{82/73} k_{SW} nt$. To get a better accuracy of the estimation, the initial part of kinetic curves were approximated by an $Ant + B(nt)^2$ function and then the A value was used for an estimation of k_{SW} . The relative detection efficiency for ions with $m/z = 73$ and $m/z = 82$ — $f_{82/73}$ was assumed equal to unity. The estimated value of k_{SW} is likely not to depend on pressure and its averaged value in the 0.2–0.6 Torr pressure range is:

$$k_{SW} = 10.3 \pm 0.5 \times 10^{-10} \text{ cm}^3/\text{s}. \quad (6)$$

The indicated error corresponds to that obtained in the points averaging procedure. The real error bar may be at least two times larger due to other sources of errors. The result demonstrates that the switching reaction is not the only channel of loss of $\text{O}_2^+ + \text{CH}_3\text{CN}$. About $30 \pm 15\%$ of the k_E value may be ascribed to k_{P1} (formation of CH_3CNH^+).

Fig. 4b shows a pressure dependence of k_F characterizing the loss of the $(\text{CH}_3\text{CN})_2^+$ ion. It follows from the figure, that k_F is pressure dependent. It may be assumed (see the kinetic scheme in Fig. 2) that one of the channels of the reaction of this ion is the association. The dependence on pressure may be presented as:

$$k_F = k_F(0) + k_0(k_s/K_d)M/[1 + (k_s/K_d)M]. \quad (7)$$

In (7), $k_F(0) = k_{P2} + k_{P3}$ corresponds to binary reactions, whose rates are not dependent on the bath gas concentration M , while the second term is an expression for the pressure dependence of the effective binary rate coefficient of the association channel $(\text{CH}_3\text{CN})_2^+ + \text{CH}_3\text{CN} + M$. k_0 is a rate constant for the formation of a complex, which can be stabilized by collisions (with a rate constant k_s); K_d is the reciprocal lifetime of the complex. The result for the fit of k_F dependence, when (7) is taken as a fitting function, is shown in Fig. 4b. Despite the large error margins of the k_0 and k_s/K_d values (see caption to the figure), the result indicates that the association reaction is an important channel for the loss of “nonprotonated” dimers. “Nonprotonated” trimer ions were actually observed in FA experiments (see Fig. 1b).

The kinetics for the formation of protonated acetonitrile and the proton-bounded dimer is complicated due to a variety of channels operative in the species production (see the scheme in Fig. 2), which results in the difficulties encountered in a quantitative treatment of the kinetic dependences. So, the kinetics will not be considered in this work. Yet, the analysis of the yield of the protonated species (based on dependences of mass spectra) shows that only 3% of their production can be ascribed to the reactions of the CH_3CN^+ precursor.

Another set of experiments has been made to study the effect of the translational energy on the reaction kinetics in

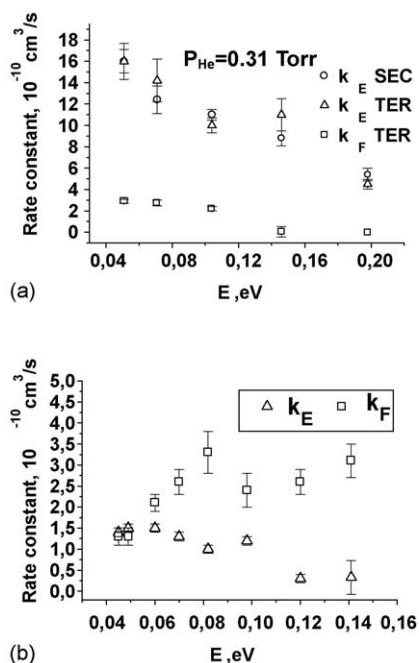


Fig. 5. (a) Energy dependences of k_F and k_E determined from kinetics of the secondary and ternary ions in the $O_2^{\bullet+} + CH_3CN$ system. (b) Energy dependences of k_F and k_E determined from kinetics of the secondary and ternary ions for the $Xe^{\bullet+} + CH_3CN$ system.

the $O_2^{\bullet+} + CH_3CN$ and $Xe^{\bullet+} + CH_3CN$ systems. Fig. 5 shows the dependences of k_E and k_F on translational energy. Their values have been determined in the fitting procedure described above. Note that the energy scale corresponds to that calculated for the collisions of primary ions with acetonitrile. The correction for the other ions may be calculated using Wanier's expression [12].

A comparison of Fig. 5a and b shows that the k_E value for the reaction $Xe^{\bullet+} + CH_3CN + CH_3CN$ is about one order of magnitude smaller than for $O_2^{\bullet+} + CH_3CN + CH_3CN$. The estimated values of k_F (for the reaction of the ternary ion $(CH_3CN)_2^{\bullet+}$) are in an agreement for the both studies.

The reason for a significant difference in k_E seems interesting. Although the bond energy of the $Xe^{\bullet+} + CH_3CN$ cluster is not known, it may be expected to be close to the energy for the $O_2^{\bullet+} + CH_3CN$ particle. The close rate coefficients of the particles formation as described in [1] may be considered as indirect evidence.

The large difference in the rate constant of the reactions $Xe^{\bullet+} + CH_3CN + CH_3CN$ and $O_2^{\bullet+} + CH_3CN + CH_3CN$ cannot be explained by the difference in the rate constants of the respective collisions, which differ by a factor of the square root of the reduced mass ratios. The difference may be related to a lower efficiency for the removal of a heavier particle from the collision complex in the former reaction or other features of a reactive behavior of the collision complex.

Due to the large dipole moment of acetonitrile, a strong alignment of particles is expected while the collision complex is being formed. Its geometry may be presented as $CH_3CN - X^{\bullet+} - NCCH_3$. The production of protonated

acetonitrile in the complex followed by its subsequent decay seems to be not efficient. This process requires a long distance migration of H to the N atom of the opposite acetonitrile particle.

The production of the stable cation radical dimer occurs only when the amount of energy removed by the particle X is large enough to prevent the subsequent "reactive decay" of the excited dimer. This energy amount has been estimated above (about 20 kcal/mol). When the molecular particle is switched from the complex, the removed energy is expected to be larger than that removed by an atomic particle due to the additional rotational and vibrational degrees of freedom of the molecule. It follows from the ratio k_{SW}/k_E that in two out of three (see (5) and (6)), the removed energy exceeds the threshold value, which is required for the formation of the stable dimer.

A similar estimation of k_{SW}/k_E for the $Xe^{\bullet+} + CH_3CN$ system has not been made due to difficulties in evaluation of the detection efficiency factor. The switching of a lower fraction of the atomic particles with high enough energy should result in a decrease of the k_{SW}/k_E ratio. Yet, no unambiguous explanation of the lower k_E may be given at present.

4. Summary and conclusions

The study of the reaction kinetics of $O_2^{\bullet+} + CH_3CN$ and $Xe^{\bullet+} + CH_3CN$ complexes with acetonitrile have shown that the production of nonprotonated dimers $(CH_3CN)_2^{\bullet+}$ in a switching reaction is an efficient channel.

The dependences of rate constants for reactions $O_2^{\bullet+} + CH_3CN + CH_3CN$ and $Xe^{\bullet+} + CH_3CN + CH_3CN$ in the 0.2–0.6 Torr pressure range at kinetic energies below 0.2 eV were studied. The rate constants of the reactions are practically independent of the buffer gas pressure. The rate constant of $O_2^{\bullet+} + CH_3CN + CH_3CN$ reaction is estimated to $(1.5 \pm 3) \times 10^{-9} \text{ cm}^3/\text{s}$ at thermal energy. Approximately 70% of the value corresponds to the switching channel. The rate constant for $Xe^{\bullet+} + CH_3CN + CH_3CN$ is about an order of magnitude smaller and equals $(1.3 \pm 0.2) \times 10^{-10} \text{ cm}^3/\text{s}$.

The main loss of "nonprotonated dimers" of acetonitrile is likely to take place in the association reaction. The effective binary rate coefficient is pressure dependent. When it is presented as $k_F = k_F(0) + k(k_s/K_d)P/[1 + (k_s/K_d)P]$, the values of the parameters are: $k_F(0) = 0.6 \pm 0.6$ and $k_0 = 5.3 \pm 1.3$ in $10^{-10} \text{ cm}^3/\text{s}$ units; $k_s/K_d = 2.3 \pm 2.2 \text{ Torr}^{-1} = (0.65 \pm 0.62) \times 10^{-16} \text{ cm}^3$.

Acknowledgments

The work was supported by Russian Foundation for Basic Research Grant No. 03-03-32443a, INTAS, Grant INTAS 93-1128 EXT and the Austrian Fonds zur Forderung der wissenschaftlichen Forschung, Project #P12429.

Appendix A. An effect of a difference in mobility and diffusion loss of primary and secondary ions on the accuracy of the estimated rate constants in the fitting procedure

The procedure, which has been used for the treatment of kinetic dependences, does not take into account the transport of ions. Such processes are described by the formalism of partial differential equations. In the applied procedure, the fitting functions are the solutions of ordinary differential equations of chemical kinetics. The approach is valid, when the diffusion coefficients and mobility are equal for different sorts of ions. The problems may arise, when the parameters differ.

An effect of a difference in charged particles transport for primary and secondary ions on the accuracy of the rate constant estimation will be considered in the section. An expression, which takes into account the processes, will be derived. The corrected expression will be used for the analysis of a possible systematic error.

The model function, which takes into account the transport processes, is derived under the following assumptions:

- The velocity profile is uniform, i.e., it is not dependent on the radial coordinate $V(r) = V_{\text{drift}} + V_{\text{flow}}$. As $V_{\text{drift}} \gg V_{\text{flow}}$, the parabolic nature of the flow velocity profile is not taken into account.
- The system of equations for ionic concentrations N_J is presented as:

$$V \frac{\partial N_J}{\partial z} = -D \Delta N_J + \phi_J(N_J), \quad (\text{A.1})$$

where z is the axial coordinate, D is the diffusion coefficient, $\phi_J(N_J)$ is an expression corresponding to dN_J/dt defined by the system of ordinary differential equations for chemical kinetics. For example, when the primary ions, whose concentration is N_0 , are reacting with an excess of the neutral reactant A, the term is $\phi_0(N_0) = -k_0[A]N_0$.

- The boundary condition for the ionic concentrations is $N_J(z, r)|_{r=a} = 0$, i.e., the ionic concentrations on a wall of the cylindrical reactor (with the radius a) are equal to zero.
- The axial diffusion is neglected, i.e., $V \partial N_J / \partial z \gg D \partial^2 N_J / \partial z^2$.
- The radial distribution of the primary ions at $z = 0$ is given by a zero order Bessel function:

$$B(r)|_{z=0} = C J_0 \left(\frac{\mu_0 r}{a} \right), \quad (\text{A.2})$$

where $\mu_0 \approx 2.4$ is the eigenvalue corresponding to J_0 . C equals $N_0|_{z=0}$, $r=0$.

As it follows from the theory of partial differential equations of the parabolic type, the solution of (A.1) for the concentration of the primary ions is given by:

$$N_0(z, r) = B(r)|_{z=0} \exp \left(-\frac{5.78 D z}{a^2 V} \right) \exp \left(-\frac{k_0 [A] z}{V} \right). \quad (\text{A.3})$$

The first exponential factor takes into account the loss due to diffusion. The argument of the exponent involves $\mu_0^2 \approx 5.78$. The other exponential factor corresponds to the loss of primary ions in the reaction.

Note that the approximated initial profile (A.2) is close to the real one, which is formed in a cylindrical reactor with the uniform velocity profile. It may be shown that, when the initial profile differs from that given by (A.2) and is approximated by a sum of the terms, which involve the higher-order Bessel functions, the contribution of the higher-order terms is decreasing with z faster than that for the zeroth-order term. It takes place because the higher-order terms involve factors $\exp(-\mu_n^2 D z / a^2 V)$. The values of μ_n are significantly larger than μ_0 (e.g., $\mu_1 \approx 5.52$ while $\mu_n \approx 2.40$). In the SIFDT apparatus, a large enough distance separates the source of the primary ions from the inlet port of the neutral reactant. So, the N_0 profile in the region, where the reaction starts is close to that given by (A.2).

The equation for the N_1 concentration (of the secondary ions) is the following:

$$V_1 \frac{\partial N_1}{\partial z} = -D_1 \Delta N_1 - k_E [A] N_1 + k_A [A] B(r) \exp \left(-\frac{5.78 D z}{a^2 V} \right) \exp \left(-\frac{k_0 [A] z}{V} \right). \quad (\text{A.4})$$

V_1 and D_1 are the velocity and diffusion coefficient of the secondary ions; k_A and k_E are the rate coefficients of their production and loss in reactions with the neutral reactant A. The solution of the equation (under the “zero boundary conditions”) is given by:

$$N_1 = B(r)|_{z=0} k_A [A] / V_1 / (k_E / V_1 [A] - k_0 / V [A]) + (5.78 / a^2) (D_1 / V_1 - D / V) (\exp(-k_0 / V [A] z) - (5.78 / a^2) (D / V) z) - \exp(-k_E / V_1 [A] z) - (5.78 / a^2) (D_1 / V_1) z. \quad (\text{A.5})$$

The expression may be simplified at a low electric field, when the Einstein relation between the ionic diffusion coefficient and mobility is valid. In this case, their ratio does depend on a sort the ion. The validity of the relation should imply $D_1 / V_1 = D / V$ and $\exp(-(5.78 / a^2) (D_1 / V_1) z) = \exp(-(5.78 / a^2) (D / V) z) = C(z)$. In this case, the concentration on the axis may be presented as:

$$N_1(0, z) = B_1(0) C(z) k_A (V / V_1) [A] / (k_E (V / V_1) [A] - k_0 [A]) (\exp(-k_0 / V [A] z) - \exp(-k_E / V_1 [A] z)) = B_1(0) f k_A [A] / (f k_E [A] - k_0 [A]) (\exp(-k_0 [A] z / V) - \exp(-f k_E [A] z / V)), \quad (\text{A.6})$$

where $f = V / V_1 \approx K / K_1 = D / D_1$ is the correction factor to k_A and k_E ; $B_1 = C(z) B(0)$. The expression is similar to (1) and (3)

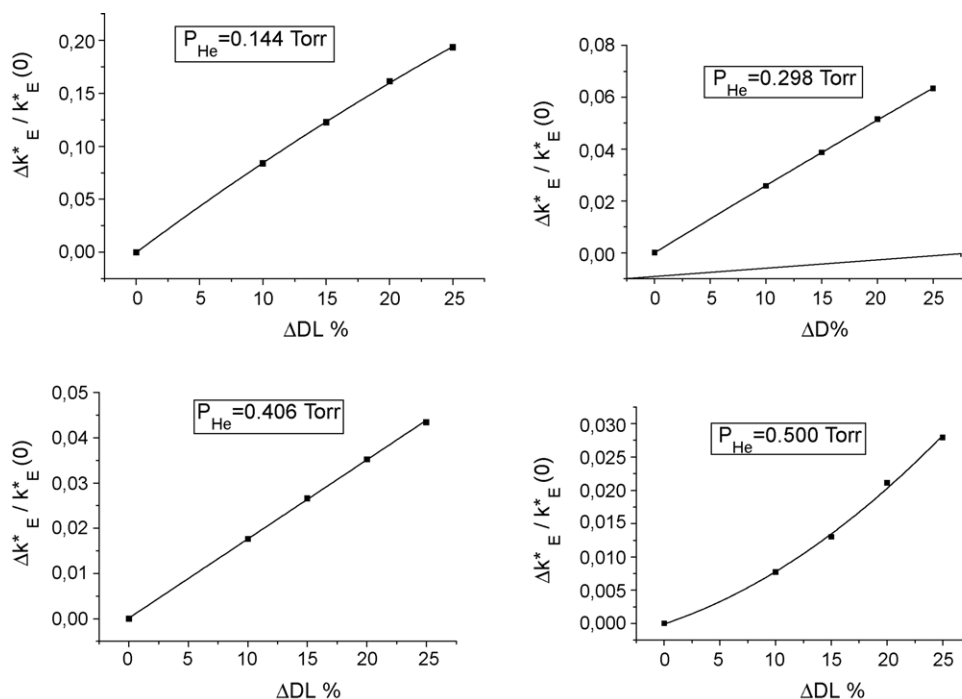


Fig. 6. An effect of a relative difference in the loss rate due to diffusion of the primary and secondary ions ΔDL (in %) on the rate constant estimation. $(k_E^* - k_E)/k_E^*$ is the relative deviation of the estimated values, when the difference is taken (*) and not taken into account.

used for the fitting procedure to determine k_E from the flow dependences (at fixed z). So, the systematic error is defined by the factor f .

When it is taken into account that the Einstein relation is only an approximation, i.e., $(5.78/a^2)(D_1/V_1 - D/V) \neq 0$, the expression for the ion current may be presented as:

$$\begin{aligned}
 I_1 = & Bfk_A[A]/(fk_E[A] - k_0[A]) \\
 & + (5.78/a^2)(D_1V/V_1 - D)(\exp(-k_0/V[A]z) \\
 & - \exp(-k_E/V_1[A]z - (5.78/a^2)(D_1V/V_1 - D)z/V)) \\
 = & Bk_A^*[A]/(k_E^*[A] - k_0[A] + \Delta K_D)(\exp(-k_0[A]t) \\
 & - \exp(-k_E^*[A]t - \Delta K_D t)), \quad (A.7)
 \end{aligned}$$

where $t = z/V$ is the drift time of primary ion, $\Delta K_D = (5.78/a^2)(D_1V/V_1 - D)$, $k_E^* = fk_E$.

The physical meaning of the value of $5.78D_i/a^2$ is an effective rate constant (in s^{-1} units) of the loss of ions due to diffusion to the walls. It depends on pressure, but not on the concentration of the neutral reactant. t may be calculated ($t = z/V$) using the reference data on mobility of the primary ions.

The expression

$$\begin{aligned}
 I_1 = & C_1/(k_E^* - k_0 + \Delta K_D/[A])(\exp(-k_0[A]t) \\
 & - \exp(-k_E^*[A]t - \Delta K_D t)) \quad (A.8)
 \end{aligned}$$

has been used as a fitting function for the available experimental dependences the $O_2^{+\bullet}CH_3CN$ ion current on the neutral

reactant concentration. Five fitting sessions for fixed values of ΔK_D being 0, 10, 15, 20 and 25% of the $5.78D_0/a^2$ value have been made at four various pressures. The results of the fitting procedures are summarized in Fig. 6. The units of the X-axis are the percentage of ΔK_D ($\Delta DL = \Delta K_D/5.78D_0/a^2 \times 100\%$); the units of the Y-axis are the relative deviation of the “corrected” k_E^* value from k_E , which has been determined, when the difference in the loss due to diffusion is not taken into account.

As it follows from the figure, the effect of the difference in ΔDL on the estimated value of k_E^* is not large at a pressure above 0.3 Torr. The main contribution to the accuracy of an estimation of k_E is likely related with a correction factor $f = V/V_1 \approx K/K_1$.

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