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Competitive association and charge transfer in the reactions of NO^+ with some ketones: a selected ion flow drift tube study

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Abstract

The rate coefficients and product ion branching ratios have been determined for reactions between NO^+ and three ketones, acetone, 2-butanone, and 3-pentanone, as a function of NO^+/reactant ketone centre-of-mass energy, E_r, and NO^+/helium carrier gas atom centre-of-mass energy, E_c, in a flowing afterglow selected ion flow drift tube apparatus. In these experiments, the helium carrier gas was maintained at a temperature of 300 K. At zero drift field, association was the dominant channel occurring at close to the collision rate forming $NO^+_.$ ketone adduct ions. At higher drift fields (E_r, $E_c < 1$ eV), charge transfer and dissociative charge transfer channels became the major channels forming fragment ions of the ketones. The decrease in the association rate coefficient with increasing E_c exhibits an inverse power law dependence $k_3 \propto E_c^{-n}$ where $n \sim 2.5$ for all three ketones. This dependence is much larger than predicted by simple theory and may be indicative of low energy vibrations contributing to the total energy pool in the $(NO_.\ ketone)^{+*}$ excited complex. (Int J Mass Spectrom 193 (1999) 35–43) © 1999 Elsevier Science B.V.

Keywords: Ion/molecule association; SIFT; Drift tube; Charge transfer

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1. Introduction

With the application of selected ion flow tube mass spectrometry (SIFT/MS) [1–3] and drift tubes [4], by using multiple ion precursors, to trace gas analysis of air and breath an interesting application of ion chemistry has been defined. These methods for trace gas analysis utilize chemi-ionization of the trace gas constituents by judiciously chosen precursor ions: most commonly used are H_3O^+, NO^+, O_2^+ (derived from moist air [1–3]), and NH_4^+ [4]. In order to interpret the product ion mass spectra it is necessary to have information on the reaction kinetics (i.e. the rate coefficients and product ions) of these precursor ions with the wide variety of trace species that are present in the air/breath samples to be analysed. Obtaining the required rate coefficients is not a straightforward process because most organic (liquid) species are adsorbed onto surfaces and so it is difficult

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to prepare mixtures of a known partial pressure, which is the usual requirement in kinetics studies. Španěl and Smith [5–9] have carried out wide-ranging investigations of the ion chemistry of H_3O^+, NO^+, and O_2^+ ions with several organic species using the SIFT technique, including some reactions with the ketones, that the present study is concerned with. In their studies, the relative rate coefficients were determined for the three ions using an air/vapour mixture of unknown partial vapour pressure, and assuming that the proton transfer reactions of H_3O^+ with the organic molecules proceeded at the collisional rate (which is readily calculated [10]). The absolute rate coefficients for the NO^+ and O_2^+ reactions were thus obtained. A large fraction of the NO^+ and O_2^+ reactions with the many organic species investigated were thus seen to proceed at or near to the collisional rate [5–9].

Ketones are common in nature and one of them, acetone (a metabolite of glucose), is present in human breath. It is with the rates, ion products, and mechanisms of the reactions of NO^+ with three ketones that this study is concerned. Španěl et al. [5] found the collisional (termolecular) association reaction:

$$NO^+ + RCOR' \xrightarrow{He} NO^+_{\cdot}RCOR'$$

to be the only reaction channel for the ketones, acetone, 2-butanone, 2-pentanone, 3-pentanone, and 2-hexanone in their SIFT at 300 K. For the larger ketones (3-hexanone, 1-phenylethanone, and menthone) charge transfer occurred in parallel with association. Their studies related to thermalized ions in helium carrier gas at a pressure close to 0.5 Torr. They invoke the phenomenon of “charge transfer complexing” to explain why the association reaction is very efficient when the ionization energy of the ketone is close to that of NO [2]. Reents and Freiser [11] had noted much earlier that the binding energy of an $NO^+_{\cdot}$ ketone complex (i.e. the NO^+ affinity) correlated with the proton affinity and the first ionization potential of the ketone. Several NO^+/ketone studies at much lower pressures than commonly used in the SIFT were carried out by Dunbar and co-workers [12–15]. They attributed the association reactions they observed at pressures up to 1×10^{-7} Torr in a Fourier transform ion cyclotron resonance (FTICR) cell, to radiative rather than collisional stabilization of the $(NO^+_{\cdot}RCOR')^*$ complexes. The rate coefficients for radiative association were relatively small [$\sim(3–6) \times 10^{-11}$ cm^3 s^{-1}] [12] and they also observed the slightly endothermic charge transfer channel to compete with association in the case of 3-pentanone [13].

In the present experimental study, we address the nature of the competition between association and charge transfer in three NO^+/ketone reactions using a flowing afterglow/selected ion flow drift tube (FA/SIFDT) where the mean kinetic energy of the NO^+ ions can be varied. The ketones chosen in this study were selected on the basis of the values of their ionization potentials (I.P.) varying from 9.70 eV for acetone to 9.31 eV for 3-pentanone converging to the ionization energy for NO of 9.26 eV.

2. Experimental

The experiments reported here were accomplished using a selected ion flow drift tube, equipped with a flowing afterglow ion source (FA/SIFDT), operating with the carrier gas in both the FA and SIFDT at room temperature (295 ± 5) K. The details of this particular selected ion flow tube have been described before [17]; the drift tube [18] and the flowing afterglow (FA) ion source are quite recent additions. The FA ion source is similar in design to that described by Van Doren et al. [19]. Other details of the modified FA/SIFDT instrument will be described elsewhere [20].

A problem in the production of NO^+ by electron impact [21] is that metastable NO^+ ($a^3\Sigma^+$) is produced in small amounts (typically $<3\%$ of total NO^+) as well as NO^+ ($X\ ^1\Sigma^+$, $v > 0$) in addition to the majority ground state NO^+ ($X\ ^1\Sigma^+$, $v = 0$). In an effort to minimise the production of these unwanted metastable and vibrationally excited NO^+ ions, the NO^+ was produced in air subjected to a microwave discharge [6]. NO^+ is formed in an air discharge predominantly by the reaction

$$N^+ + O_2 \rightarrow NO^+ + O \quad (1)$$

Table 1
Rate coefficients and product ion branching ratios at zero field from NO^+ with acetone, 2-butanone, and 3-pentanone

Ketone	Branching ratio	Product	k_{obs} [a] (10^{-9} cm^3 s^{-1})	k [b] (10^{-9} cm^3 s^{-1})	k [c] (10^{-9} cm^3 s^{-1})	k_{coll} [d] (10^{-9} cm^3 s^{-1})	ΔIP (eV) [e]
CH_3COCH_3	1.0	$NO^+ \cdot CH_3COCH_3$	1.3	1.2	0.003	3.3	−0.44
$C_2H_5COCH_3$	1.0	$NO^+ \cdot C_2H_5COCH_3$	2.1	2.8	0.027	3.2	−0.26
$C_2H_5COC_2H_5$	0.95	$NO^+ \cdot C_2H_5COC_2H_5$	2.6	3.4	0.18	3.3	−0.05
	0.05	$C_2H_5COC_2H_5^+$					

[a] Present study; at a pressure of 0.44 Torr of helium.

[b] Previous SIFT study [5]; at a pressure of 0.50 Torr of helium.

[c] At a pressure of $<1 \times 10^{-7}$ Torr; these results from [12] and [13] are for bimolecular association only.

[d] Collisional rate coefficients [10].

[e] See [16].

Metastable and vibrationally excited NO^+ are then quenched by N_2 [22,23]. Without taking these precautions, the presence of $(NO^+)^*$ species formed from the discharge was apparent by the observation at zero electric field (in the SIFDT) of small product ion signals corresponding to dissociative charge transfer reactions with the ketones, reactions that cannot occur with ground state NO^+ on thermodynamic grounds. The small amount of $(NO^+)^*$ in some experiments in this study (<3%) did not influence the observed rate coefficients in any significant way.

In the present work, rather than calibrating the rate coefficients relative to the rate coefficients for proton transfer from H_3O^+ as Španěl et al. report [5], we were able to measure the absolute flow rates of the three chosen ketones in the usual way by monitoring the decrease in pressure of a known volume of ketone vapour [17].

3. Results and discussion

The reactions of NO^+ with the three ketones, acetone, 2-butanone, and 3-pentanone, were examined as functions of the NO^+–ketone (E_r) and the NO^+–He (E_c) centre-of-mass energies. As noted previously, NO^+ reacts with ketones at thermal energies generally via association. The NO^+–ketone binding energies are known and are substantial as can be inferred from the rapid association rate coefficients observed. The binding energies are (in electron volts) [13]: $(CH_3)_2CO$, 1.77; $CH_3COC_2H_5$, 1.82; $(C_2H_5)_2CO$, 1.85. If the ketone has an ionization energy close to or lower than that of NO (9.26 eV) [16] then charge transfer may also occur.

The data from the earlier SIFT study of Španěl et al. [5] are compared with the results from the present study at zero field in Table 1. We note the acceptable agreement in the results of these two studies, which is pleasing in view of the very different methods used to monitor the ketone flows and hence to obtain the rate coefficients. In these three reactions charge transfer is endothermic, but for the 3-pentanone reaction it is only marginally so (0.05 eV) and in fact a small fraction of charge transfer (5%) was observed in the present study at thermal energies (zero E field). As the centre-of-mass energies between the reactant ion and the reactant molecule, E_r, and the reactant ion and the carrier gas atoms, E_c, are increased, endothermic charge transfer becomes energetically possible. Exploring the influence of E_c and E_r in the SIFDT provides a means of examining the nature of the competition between association and charge transfer in these reactions. Although it is of course not possible to vary E_c and E_r independently of each other, it is still important to identify their different characteristics.

3.1. Drift field measurements

Ions drifting through a gas under the influence of a uniform electric field gain translational energy from the electric field and lose energy in collisions with the bath gas (helium) and reactant gas (ketone). Ultimately the energy gain and loss processes approach equilibrium and the ions drift through the gas with a velocity v_d that depends on the ratio E/N (E = electric field strength and N = carrier gas number density). The kinetic energy of the ions, $\mathrm{KE_{ion}}$, is then given by the Wannier formula [24]

$$\mathrm{KE_{ion}} = \frac{3}{2}k_BT + \frac{m_iv_d^2}{2} + \frac{m_cv_d^2}{2} \tag{2}$$

where m_i is the mass of the ion, m_c is the mass of the carrier gas atoms, and k_B is the Boltzmann constant. Eq. (2) in the centre-of-mass frame becomes [25]

$$E_r = [(m_r/(m_i + m_r)]\ (\mathrm{KE_{ion}} - \tfrac{3}{2}k_BT) + \tfrac{3}{2}k_BT \tag{3}$$

where E_r is the mean ion-reactant gas centre-of-mass energy, and m_r is the reactant neutral (ketone) mass. Similarly E_c, the mean ion-carrier gas atom centre-of-mass energy, is given by

$$E_c = [m_c/(m_i + m_c)]\ (\mathrm{KE_{ion}} - \tfrac{3}{2}k_BT) + \tfrac{3}{2}k_BT \tag{4}$$

Because collisions of $\mathrm{NO^+}$ with the helium carrier gas are much more frequent than collisions with the ketone, it is E_c that determines the internal energy state of the molecular ions prior to their interaction with the reactant ketone molecules. Similarly, it is the distribution E_r that describes the mean relative translational energy between the $\mathrm{NO^+}$ ions and the ketone molecules.

As a consequence the temperature of the reactant ions is not clearly defined except at very low electric fields and their translational and internal energy distributions will not be Maxwell-Boltzmann. Thus a true thermodynamic ion temperature cannot be defined. Based on the simple model for three-body association reactions exemplified by the $\mathrm{NO^+}$ reaction with acetone:

$$\mathrm{NO^+} + \mathrm{CH_3COCH_3} \underset{k_{-1}}{\overset{k_f}{\rightleftharpoons}} (\mathrm{NO^{+}\cdot CH_3COCH_3})^*$$
$$\xrightarrow{k_r} \mathrm{NO^{+}\cdot CH_3COCH_3} + h\nu \tag{5}$$

$$(\mathrm{NO^{+}\cdot CH_3COCH_3})^* + \mathrm{M}$$
$$\xrightarrow{\beta k_s} \mathrm{NO^{+}\cdot CH_3COCH_3} + \mathrm{M} \tag{6}$$

Adams and Smith [26] have proposed that a "temperature," T_c, may be assumed for the association complex, such that T_c may be equated to T_i (the internal temperature of the ion which is defined by E_c) or T_t (the translational temperature of the ion relative to the reactant neutral when $E_r > E_c$ as is the case for the reactions in this study). This model predicts the temperature variation for k_3, the rate coefficient for the termolecular reaction, as

$$k_3 \propto (T_c^{r_c/2})/(T_t^{3/2}T_i^{r_i/2}T_n^{r_n/2}) \tag{7}$$

where r_c, r_i, r_n are, respectively, the numbers of rotational degrees of freedom in the complex (c), the reactant ion (i), and the reactant neutral (n). The T values are their associated temperatures defined by $T_c = T_t$, $(3/2)k_BT_t = E_r$, and $(3/2)k_BT_i = E_c$. $\mathrm{NO^+}$ possesses only two rotational degrees of freedom, and thus for its reaction with nonlinear polyatomic molecules like acetone, Eq. (7) becomes

$$k_3 \propto E_c^{-1.0} \tag{8}$$

This model will be applied to the present data in the following sections.

3.2. $\mathrm{NO^+}$ + *acetone*

Association is the main process observed in this system under all conditions of the applied drift field in the SIFDT:

$$\mathrm{NO^+} + \mathrm{CH_3COCH_3} \xrightarrow{\mathrm{He}} \mathrm{NO^{+}\cdot(CH_3)_2CO} \tag{9}$$

At the highest accessible drift fields, a minor charge transfer channel is evident; this is 0.44 eV endothermic for ground state reactants and even at an $E_r = 0.8$ eV represents a very small (insignificant) channel. At zero field, the observed pseudobimolecular rate coefficient, k_{2obs}, for this *termolecular* association reaction is invariant with pressure over the restricted range from 0.25 and 0.70 Torr at a value of 1.3×10^{-9} cm^3 s^{-1}, which is 40% of the collisional rate coefficient k_c (Table 1). From simple reasoning it would be expected that "pressure saturation," i.e. a pressure invariant k_{2obs}, would coincide with k_c, but this condition is clearly not achieved at the pressures accessible in these experiments. Whether the apparent pressure invariance indicates that a small but gradual increase of k_2 with pressure would occur, or whether pressure saturation has been achieved with a rate coefficient less than k_c, is not clear. If the latter case is applicable, and there is precedence for this, then there are several possibilities that may be responsible including spin statistics [27] or a double potential-well model [28,29]. In the double-well model, the short mean lifetime of the loosely bound complex means that the "pressure saturation" regime in which the tightly bound complex is formed corresponds to a rate coefficient less than the collision rate [28].

To seek for an understanding of this NO$^+$/acetone association reaction, we examined it at different E_c and E_r in the SIFDT. The variations of log(k_{3eff}), (where k_{3eff} is the effective termolecular association rate coefficient derived from $k_{3eff} = k_{2obs}$/[He]), with both log E_c and log E_r, are shown in Fig. 1(a). Both plots show a decrease in k_{3eff} with increasing ion energy as expected if the [NO.(CH$_3$)$_2$CO]$^{+*}$ lifetime against unimolecular dissociation decreases with increasing internal energy of the excited collision complex. Further, as E_r increases, k_{2obs} reduces below its saturation value allowing meaningful values of the association rate coefficients, k_3, to be determined. As an example, the variation in k_{2obs} with helium pressure at $E_r = 0.43$ eV is shown in Fig. 1(b). The near linear dependence indicates that the reaction has moved out (or almost out) of the near pressure saturation regime and a linear least squares fit to the data yields $k_3 = 1.2 \times 10^{-26}$ cm^6 s^{-1} at $E_r = 0.43$ eV. Thus we find that $k_{3eff} \geq 9.1 \times 10^{-26}$ cm^6 s^{-1} at zero field (derived from the observed rate coefficient of 1.3×10^{-9} cm^3 s^{-1} at 0.44 Torr) and $k_3 \sim 5.7 \times 10^{-27}$ cm^6 s^{-1} at $E_r = 0.88$ eV (derived from the variation in rate coefficient measured at $E_r = 0.88$ eV).

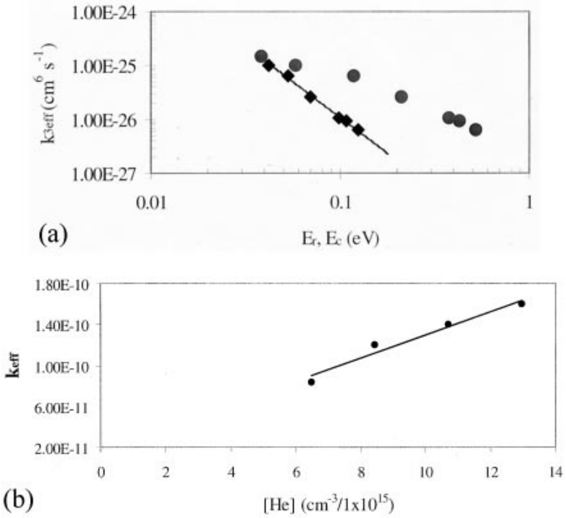

Fig. 1. (a) The variation in ln(k_{3eff}) for NO$^+$ and acetone with log(E_r/eV) (closed circle) and log(E_c/eV) (closed square) obtained at a pressure of 0.30 Torr. (b) The variation in k_{eff} for NO$^+$ and acetone with helium density at $E_r = 0.43$ eV. The linear fit yields an association rate coefficient for termolecular association of $k_3 = 1.2 \times 10^{-26}$ cm^6 s^{-1}.

The slope of the least squares line in Fig. 1(a) of log k_{3eff} against log E_c is -2.5, which is obviously greater than the slope of -1.0 predicted in Eq. (8). We discuss possible reasons for this difference after the results for the 2-butanone and 3-pentanone reactions are presented.

One problem specific to the NO$^+$/acetone reaction studies was encountered. At higher values of E_r, the effective bimolecular rate coefficient dropped to less than 10^{-10} cm^3 s^{-1} and linear semilogarithmic decays of ln I_{NO^+} against acetone flow could not be maintained. A probable reason for the nonlinearity with the high flows of acetone that are required is that the NO$^+$ ion mobility changes from its value in pure helium.

3.3. NO$^+$ + 2-butanone

At thermal energies, the only product of this reaction is the adduct, $NO^+ \cdot CH_3COC_2H_5$, but additionally at higher energies in the SIFDT, ion products resulting from charge transfer and dissociative charge transfer appear:

$$NO^+ + CH_3COC_2H_5 \xrightarrow{He} NO^+ \cdot CH_3COC_2H_5 \tag{10a}$$

$$\rightarrow CH_3COC_2H_5^+ + NO - 0.26\text{ eV} \tag{10b}$$

$$\begin{gathered} \rightarrow CH_3CO^+ + C_2H_4 + HNO - 0.64\text{ eV} \\ (\text{or } CH_3CO^+ + CH_3CHNOH + 1.15\text{ eV}) \end{gathered} \tag{10c}$$

$$\rightarrow C_2H_5CO^+ + (CH_3NO) + 0.86\text{ eV} \tag{10d}$$

The association reaction apparently proceeds in the pressure saturation regime at thermal energies ($k_{3\mathrm{eff}} > 1.8 \times 10^{-25}$ cm^6 s^{-1}) with $k_{3\mathrm{eff}}$ decreasing at higher energies (at $E_r = 0.89$ eV, $k_{3\mathrm{eff}} = 7.6 \times 10^{-27}$ cm^6 s^{-1}). A plot of ln $k_{3\mathrm{eff}}$ versus E_c and E_r shown in Fig. 2(a) indicates the energy dependence of the association channel. Like the acetone association reaction, the linear least squares fit of ln $k_{3\mathrm{eff}}$ against ln E_c yields a slope of −2.3 [Fig. 2(b)], considerably in excess of the value of −1.0 predicted by Eq. (8). The departure from linearity at low E_c values again indicates the approach to pressure saturation.

Nondissociative charge transfer producing $C_4H_8O^+$ ions, which is endothermic by 0.26 eV for ground state reactants at thermal energy, onsets near to threshold [see Fig. 2(b)] and then becomes increasingly important with increasing E_r to become dominant at $E_r = 0.89$ eV where the partial rate coefficient for this channel is 1.0×10^{-10} cm^3 s^{-1}. For comparison, at the same E_r the bimolecular rate coefficients corresponding to the other channels are $k_{10a} = 9.8 \times 10^{-11}$ cm^3 s^{-1}, $k_{10c} = 2.0 \times 10^{-11}$ cm^3 s^{-1} and $k_{10d} = 3.0 \times 10^{-11}$ cm^3 s^{-1} [see Fig. 2(b)]. Because there are onsets of the reactive channels in Eq. (10) this suggests that these reaction channels are endothermic. However it cannot be ruled out that barriers may exist for exothermic channels requiring extensive rearrangements [Fig. 2(b)]. Indeed the neutral products indicated are not necessarily

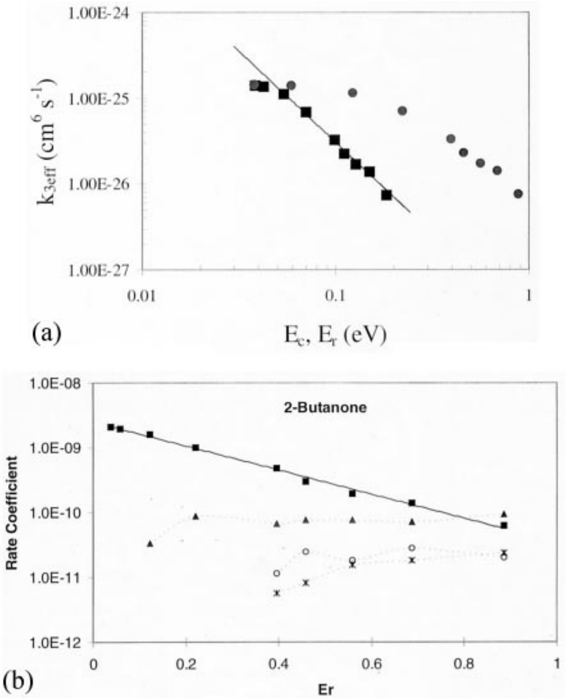

Fig. 2. (a) The variation in ln($k_{3\mathrm{eff}}$) for NO$^+$ + $CH_3COC_2H_5$ with log(E_c/eV) (closed square) and log(E_r/eV) (closed circle). The slope of the least squares line of best fit for log E_c is −2.5. (b) Rate coefficients for the NO$^+$ + $CH_3COC_2H_5$ reaction at different values of E_r. [$NO^+ \cdot C_4H_8O$ (closed square); $C_4H_8O^+$ (closed triangle); $C_2H_5CO^+$ (open circle); CH_3CO^+ (cross).] The solid line is the least squares minimized regression line for the association channels.

correct as the experiment does not provide information on product neutrals.

A decrease in the lifetime of the complex with increasing energy is implied from the decrease in rate coefficient of the association channel (10a). The total rate coefficient for the binary reactions (10b)–(10d) is only 1.5×10^{-10} cm^3 s^{-1} at the highest attainable E_r. That the k_2's do not reach the appropriate k_c, suggests that charge transfer occurs within the reaction complex, the lifetime of which continuously decreases with increasing E_r. Thus, the k_2 values observed at higher energies are a reflection of the increased efficiency of charge transfer and the decreasing efficiency of the reaction with decreasing complex lifetime. (Stated another way, even though charge transfer is favoured by increasing E_r it is inhibited by the decreasing complex lifetime.) It is interesting to note that identical charge transfer and dissociative charge transfer product ions result from the O_2^+ reaction with 2-butanone [5].

3.4. NO^+ + 3-pentanone

As previously mentioned, at thermal energies the major product for this reaction is association but charge transfer and dissociative charge transfer become dominant at higher energies [Fig. 3(a)].

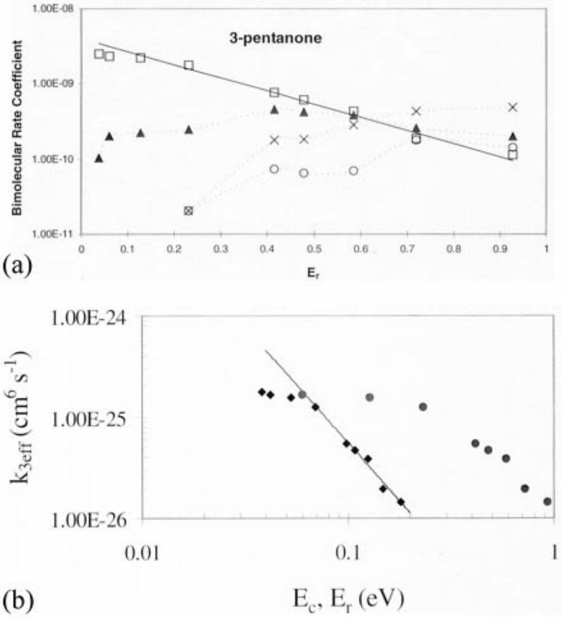

Fig. 3. (a) Rate coefficients for the $NO^+ + (C_2H_5)_2CO$ reaction at different values of E_r. [$NO^+ C_5H_{10}O$ (closed square); $C_5H_{10}O^+$ (closed triangle); $C_2H_5CO^+$ (open circle); $C_2H_4CO^+$ (cross).] The solid line is the least squares minimized regression line for the unsaturated region of the association channel. (b) The variation in $\ln(k_{3\mathrm{eff}})$ for $NO^+ + (C_2H_5)_2CO$ with $\log(E_c/\mathrm{eV})$ (closed square) and $\log(E_r/\mathrm{eV})$ (closed circle). The slope of the least squares line of best fit is -2.3.

$$NO^+ + (C_2H_5)_2CO \rightarrow NO^+\!\cdot(C_2H_5)_2CO \tag{11a}$$

$$\rightarrow (C_2H_5)_2CO^+ + NO - 0.05\ \mathrm{eV} \tag{11b}$$

$$\rightarrow C_2H_5CO^+ + C_2H_4 + HNO - 0.17\ \mathrm{eV}\ (\text{or } C_2H_5O^+ + C_2H_5NO + 1.4\ \mathrm{eV}) \tag{11c}$$

$$\rightarrow C_2H_4CO^+ + C_2H_6 + NO - 0.40\ \mathrm{eV} \tag{11d}$$

$k_{3\mathrm{eff}}$ decreases from $\geq 1.7 \times 10^{-25}$ cm^6 s^{-1} at thermal energies to $k_3 \sim 1.5 \times 10^{-26}$ cm^6 s^{-1} at $E_r = 0.93$ eV as it is shown in Fig. 3(b). The power law dependence again exhibits a significantly different exponent value (-2.3) from that predicted by Eq. (8) of -1.

The binary rate coefficient k_2 for the nondissociative charge transfer channel (11b) increases from $k_{11\mathrm{b}} = 1.0 \times 10^{-10}$ cm^3 s^{-1} at thermal energy reaching a maximum of 4.3×10^{-10} cm^3 s^{-1} at $E_r = 0.50$ eV and then falls to $k = 2.0 \times 10^{-10}$ cm^3 s^{-1} at $E_r = 0.93$ eV as the dissociative charge transfer channels resulting in $C_2H_5CO^+$ ions becomes dominant as can be seen in Fig. 3(a). Again, the various channels exhibit clear onsets at finite E_r either because they are endoergic or because of the existence of energy barriers on the potential surface.

3.5. Variation of ln k_3 with ln E_c

In accordance with the simple model proposed by Adams and Smith, which appears to be valid for the association reactions of CH_3^+ ions with some diatomic molecules [26], the termolecular rate coefficient for association exhibits an inverse power law dependence with E_c. However, the power law indices observed in all three NO^+/ketone reactions are about -2.5 [Figs. 1(a), 2(a), and 3(b)], i.e., obviously larger than the -1.0 value predicted by the model. Possible reasons for this large discrepancy are that more energy enters the complex than is predicted by Eq. (7) hence reducing its lifetime and/or the complex "temperature" T_c is not correctly approximated by T_t. Could vibrational excitation of the reactant NO^+ be a factor? This is unlikely in these experiments. Pogrebnya et al. [21] have measured quenching rate coefficients, k_q, for NO^+ ($v = 1$) in a helium carrier gas as a function of E_c. The maximum value of E_c attained in the present experiments was 0.2 eV, which is less than 0.3 eV where Pogrebnya et al. report a rate coefficient of $k_q \sim 3 \times 10^{-14}$ cm^3 s^{-1} for the quenching reaction

$$NO^+ \ (v \geq 1) + \ He \rightarrow NO^+ \ (v = 0) + \ He \qquad (12)$$

Assuming that equilibrium is achieved between excitation and de-excitation in these SIFDT experiments, then the quenching and excitation rates are related according to

$$k_{ex} = k_q \exp(-E/k_B T) \qquad (13)$$

where E represents the vibrational energy of the NO^+ ions. The vibrational energy of $NO^+(v = 1)$ is 0.29 eV and hence by using Eq. (13) we deduce that $k_{ex} \sim 3 \times 10^{-19}$ cm^3 s^{-1} at 0.3 eV from the Pogrebnya et al. value of k_q. In our experiment at a helium pressure of 0.5 Torr and a reaction time of ~1 ms, the fraction of $NO^+(v = 1)$ produced at $E_c = 0.2$ eV is therefore very much less than 0.1%.

If vibrational excitation of NO^+ is not a factor in accounting for the enhanced dependence of log k_{3eff} upon log E_c then what is? One possible explanation is that low frequency vibrations and internal rotations in the ketone molecules may contribute to a shortening of the lifetime of the (NO^+ ketone)* excited complex at higher E_c values. We note that although the neutral vibrational energy is not changing in these experiments, it still adds to the energy resident within the complex where additional energy induced by collisions is accumulated. Bass and Jennings [30] noted that divergence from simple T^{-n} variations in k_3 (for association reactions of CH_3^+ with diatomic and triatomic molecules) tend to be largest when the reaction intermediate complex has a deep well as occurs in the present case, and a number of the low frequency vibrations and internal rotations of the complex are populated.

4. Concluding remarks

We have examined the variations of the rate coefficients for competing three-body association and charge transfer in the reactions of NO^+ with the ketones, acetone, 2-butanone, and 3-pentanone, with the centre-of-mass interaction energies E_c and E_r. In all three reactions, association is dominant and efficient at thermal energies and indicative of the formation of bound complexes $(NO.RCOR')^+$ which may well correspond to the formation of derived nitrite $[R(CONO)R']^+$ cations by the addition of NO^+ to the carbonyl oxygen. Preliminary ab initio calculations appear to support this premise [31]. The lifetimes of the $(NO.ketone)^{+*}$ excited intermediate ions are clearly sensitive to the NO^+–ketone interaction energies as is manifest by the rapid decrease in the association rate with both E_r and E_c. The independence of k_{2obs} with pressure at thermal energies for the NO^+–acetone reaction, at a rate coefficient only 40% of the collision rate coefficient, opens the possibility of a double well potential surface model describing the association as has been proposed previously for other association reactions [28,29,32].

As noted earlier, the model utilized to account for the dependence of the rate coefficient for association E_c [26], led to a predicted inverse power law dependence for the log k_3 versus log E_c plots. Although the index of these plots was remarkably similar for all three ketones examined in this study (~ -2.5), it was considerably larger than the value of -1.0 anticipated from the simple model, which it must be stressed, did not consider the role of any vibrational excitation in either the ionic or the neutral reactants. It is worth noting that the model successfully predicted the power law for CH_3^+, a polyatomic ion with diatomic molecules having relatively high frequency vibrations. In the present case the ion is diatomic and the neutral reagent is polyatomic. As a consequence a reasonable explanation for the difference between the present experimental results and the predictions of this simple model are that energy accumulation within low frequency inverse rotations and vibrations may be crucial in complexes comprising large reactant molecules such as ketones. How energy is utilized in such ion-molecule complexes to overcome a reaction endothermicity (to charge transfer and dissociative charge transfer) is an interesting question. Are all forms of energy equally efficient at overcoming the reaction endothermicity? Viggiano and Morris [33] using a variable temperature SIFDT have shown that the rotational temperature of the reactant molecule and the translational energy of the ion may both be utilized in specific reactions. The present experiments indicate that the translational energy of the NO^+ ions is efficiently accommodated into the $NO^+_{\cdot}$ ketone complexes which both reduces the association efficiency and is utilized to open endothermic charge transfer channels.

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