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Radiative Association of NO^+ with 3-Pentanone: Rate, Binding Energy, and Temperature Dependence

Victor Ryzhov, Stephen J. Klippenstein,* and Robert C. Dunbar*

Contribution from the Chemistry Department, Case Western Reserve University,
Cleveland, Ohio 44106

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Abstract: Measurements were made of the radiative association kinetics of NO^+ with 3-pentanone as a function of temperature from 300 to 400 K, using the Fourier-transform ion cyclotron resonance ion-trapping mass spectrometer. Both the absolute association rate and the temperature dependence were compared with the predictions of two levels of theory, a simple RRKM-based approach previously applied to several systems, and a new, detailed variational transition state theory (VTST) approach incorporating *ab initio* calculations of vibrational frequencies and IR emission intensities. The analysis by the VTST approach was considered reliable and successful enough to justify averaging with a previous thermochemical determination to give a revised binding energy for the complex of 41.6 ± 2 kcal mol^{-1} (1.80 ± 0.1 eV). The VTST approach also gave excellent agreement with the observed temperature dependence. The RRKM estimate of the rate was in satisfactory agreement with observation, but the slope of the temperature dependence plot predicted by this simple theory was slightly too steep. The competing endothermic charge transfer channel, whose rate was observed to increase slightly with temperature, was included in the VTST modeling. The combination of radiative association kinetic data with *ab initio* calculations and VTST modeling as done here appears promising as a new route to ion-neutral complexation thermochemistry.

Introduction

The process of dissociation of a gas-phase ion into an ionic plus a neutral fragment has received a great deal of attention, leading among other things to the extensive determination of ion−neutral binding energies. Only recently has the converse process of ion−neutral association been recognized as having promise for accurate bond energy determinations. This reflects the evolution of adequate theoretical understanding for confident quantitative interpretation of association experiments. In particular, the radiative association process is susceptible to thorough quantitative analysis, potentially leading to thermochemical information of useful quality. The present study of the radiative association reaction of pentanone with NO^+ offers a good illustration, as well as a testing ground, for recent advances in understanding of such rates and temperature dependences, leading to more confidence in the assignment of binding energies from the kinetic analysis.

Radiative association, i.e., the sticking together of an ion and a neutral molecule in the gas phase with stabilization of the collision complex by photon emission, is an important part of the chemistry of interstellar molecule building[1] as well as a common process in ion-trapping experiments. Recent reviews have collected results for smaller[2] and larger[3] systems. The overall association reaction is

$$A^+ + B \xrightarrow{k_2} A^+B \qquad (1)$$

where k_2 is the apparent bimolecular rate constant, and A^+B is a complex which has lost enough internal energy to become stabilized with respect to redissociation.

This rate constant is expected to depend strongly on the temperature. Temperature dependence of radiative association rates has been recognized and well-studied for small systems (3−10 atoms).[1,2] For relatively large systems (10−30 atoms), however, only a few results have been reported,[4−7] and theoretical interpretation has not been very profound or incisive.[5,6,8,9] (There has, on the other hand, been deeper theoretical consideration of the temperature dependence of the related collisional association process.[10−13]) The present work has the two purposes of describing a more detailed and confident theoretical analysis than has been previously used in such studies and of applying this analysis to new data for the NO^+/pentanone system to reexamine the bond strength of this complex.

It was thought that (NO^+·pentanone) was a complex whose binding energy was particularly well-known from the accurate equilibrium measurements of Reents and Freiser,[14] and it was expected that the result of the present careful temperature dependent study would be a validation of our ability to correlate radiative association kinetics with binding energies. As will be seen below, however, the present results led to the recognition that the absolute anchor of Reents and Freiser's binding energy

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* Authors to whom correspondence should be addressed.

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scale needed to be revised, so that a further result of the present study is a revision of the previous thermochemistry of this complex.

The NO$^+$/pentanone system was attractive for careful study for several reasons: first, its binding energy was considered quite well-known (2.09 eV) from the equilibrium thermochemical work of Reents and Freiser;[14] second, previous study of the reaction at room temperature showed reasonably fast association;[15] and third, there is added interest because of the presence of a reactive (charge transfer) channel competitive with complex stabilization. It is of particular interest to look at the temperature dependences of these two competing reaction channels. The complete reaction scheme is

$$C_5H_{10}O + NO^+ \rightarrow [C_5H_{10}O{\cdot}NO^+]^* \rightarrow C_5H_{10}O{\cdot}NO^+ \qquad (2)$$

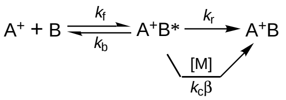
$$\rightarrow C_5H_{10}O^+ + NO \qquad (3)$$

$$\rightarrow C_5H_{10}O + NO^+ \qquad (4)$$

where $[C_5H_{10}O{\cdot}NO^+]^*$ is the metastable collision complex.

Kinetic Considerations

Mechanism. Reaction 1 can be analyzed in terms of the detailed mechanism 5:



(5)

where k_f is the bimolecular rate constant for the collisional complex formation, k_b is the unimolecular redissociation rate constant, k_r is the unimolecular rate constant for IR photon emission from A^+B^*, $k_c\beta$ is the bimolecular rate constant for collisional stabilization of A^+B^* by collision with neutral M, and β is the collisional stabilization efficiency. This mechanism gives the following expression for k_2:

$$k_2 = k_f k_r/(k_b + k_r) + k_f k_c \beta k_b [M]/(k_b + k_r)^2 \qquad (6)$$

At low pressures when three-body collisional stabilization of the complex is negligible, k_2 becomes k_{ra}, the bimolecular rate constant for radiative association, and the kinetics simplifies:[8,16]

$$k_2 = k_{ra} = k_f k_r/(k_b + k_r) \qquad \text{(low-pressure limit)} \qquad (7)$$

Since k_2 can be measured directly, the low-pressure experiments give the radiative association constant.

Since the metastable complex A^+B^* is in a highly nonuniform and non-Boltzmann distribution of internal energies and angular momenta, the above kinetic picture in terms of rate constants is only approximate. (Or, in other words, as the conditions of pressure, reaction time, and so forth are varied, the rate constants in the kinetic scheme of eq 5 actually vary in their numerical values, and the application of eqs 6 and 7, assuming them to be true constants, is not strictly correct.) A growing body of experience suggest that the simple kinetic model underlying eqs 6 and 7 is actually quite a good approximation. However, one purpose of the more detailed kinetic analysis used here is to describe the fully energy- and angular momentum-resolved kinetic framework needed to treat the kinetics of eq 5 correctly.

Modeling Predictions. We applied two levels of theoretical sophistication to calculating the rate and temperature dependence of this association reaction. One of these, combining low-level RRKM dissociation theory with generic estimates of radiative transition probabilities, was described in detail in refs 8 and 9. The other, combining variational transition-state theory (VTST) with *ab initio* vibrational frequencies and IR intensities for the association complex, represents our ongoing effort to formulate and apply the most detailed and accurate theoretical approach which is feasible for systems this large.

(a) RRKM Approach. The overall association rate depends on three factors:

(i) The first is the rate of formation of the energized complex (k_f). The rate constant was taken as equal to the orbiting rate constant k_{orb}. Using values of 10.5 Å^3 for the polarizability[17] and 2.7 D for the dipole moment, respectively, of 3-pentanone, the trajectory modeling of Su and Chesnavich[18] gives a value of the orbiting constant of 3.2×10^{-9} cm^3 molecules^{-1} s^{-1}. The weak temperature variation of k_{orb} was ignored in the calculations of association efficiency given below.

(ii) The second is the rate of IR photon emission from the energized complex (k_r). We used the value predicted for a "standard hydrocarbon" as an approximation.[8] The weak temperature dependence of k_r was ignored.

(iii) The third is the redissociation rate of the collisional complex (k_b). It has been found[3,8,9,15,19] that simple RRKM theory can be applied in a number of systems to give rough estimates of association efficiency in surprisingly good agreement with experiment. In keeping with the simplified nature of this treatment, the frequency sets used in these RRKM-derived estimates were those of the generic "standard hydrocarbon" model[8], with frequencies of the transition state assigned to give a $\Delta S^{\ddagger}_{1000K}$ of +15 cal K^{-1}. In the present case, this approach was used to calculate k_b for various temperature values spanning the range of the experiments.

Once we obtained all three components eq 7 was used to give theoretical values for the radiative association rate constant. For this low level of theoretical modeling, the charge-transfer reaction channel was assumed not to affect the efficiency of radiative association significantly. This assumption is shown to be reasonable by the more detailed modeling described below.

(b) Transition State Theory Approach. The detailed transition-state calculation of the temperature-dependent k_{ra} breaks into two parts. One component of this calculation is the estimation of the rate of radiative stabilization of the energized collision complex by IR photon emission using the *ab initio* frequencies and intensities of the vibrational modes. The calculation of the IR photon emission rate in this way is straightforward, and has been described.[20] The needed vibrational frequencies and IR intensities were calculated as described in the next section. The *ab initio* frequencies and intensities found for this complex and used in the kinetic modeling are given in Table 1. The IR emission rate is weakly dependent on the internal energy of the complex, and accordingly was calculated for each energy in the energy-resolved VTST modeling. As an indication of the order of magnitudes involved, we can note that the average internal energy of the collision

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Table 1. Calculated Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities (parentheses) (km mol^{-1}) for the (NO^+·Pentanone) Complex[a]

33.7 (0.01), 48.6 (0.38), 62.6 (3.6), 71.9 (13), 100 (16), 170 (42), 242 (9.6), 248 (41), 273 (0.45), 285 (6.3), 393 (46), 438 (9.9), 503 (2.0), 681 (18), 763 (0.14), 857 (11), 892 (13), 1027 (8.9), 1095 (6.4), 1109 (3.6), 1119 (2.8), 1211 (15), 1249 (51), 1257 (4.9), 1385 (0.3), 1443 (1.5), 1514 (0.09), 1550 (19), 1568 (25), 1573 (3.6), 1587 (1.8), 1599 (28), 1641 (9.2), 1644 (13), 1644 (5.8), 1650 (11), 1897 (438), 2760 (307), 3203 (12), 3213 (23), 3216 (8.1), 3228 (19), 3239 (2.4), 3250 (0.15), 3277 (40), 3298 (31), 3303 (13), 3305 (20)

[a] The five low-frequency transitional mode frequencies given here have been adjusted downward by a factor of 1.4 from the Hartree–Fock results, as justified in the text. Note that all of the Hartree–Fock frequencies given here were scaled by 0.89 for use in the kinetics calculations.

complexes is about 2.0 eV (assuming a zero-Kelvin binding energy of about 1.8 eV), and the rate of IR photon emission at this energy is calculated to be of the order of 40 s^{-1}.

The other component of the k_{ra} calculation is the kinetics of formation and redissociation of the collision complex. These kinetics were treated by a variational transition state theory (VTST) approach incorporating convolutions over a thermal distribution of energies and angular momenta of the reactants and over the distribution of angular momenta and energies of the complex.[13] The expression for k_{ra} within transition-state theory is

$$k_{\text{ra}} = \frac{1}{hQ_{\text{reactants}}} \int\int \mathrm{d}E\, \mathrm{d}J\, N_{EJ} \mathrm{e}^{-E/kT} \times \left\{ \frac{k_{\text{r}}(E,J) + k_{\text{c}}(E,J)[\text{M}]}{k_{\text{b}}(E,J) + k_{\text{r}}(E,J) + k_{\text{c}}(E,J)[\text{M}]} \right\} \tag{8}$$

where $Q_{\text{reactants}}$ is the canonical partition function for separated reactants, and N_{EJ} is the number-of-states function for the variational transition state separating reactants from complexes. The collision rate constant k_{c} was taken from the trajectory calculations of Su and Chesnavich, assuming that each orbiting collision stabilizes the metastable complex, and was estimated as 2.2×10^{-9} cm^3 molecules^{-1} s^{-1}.[18]

A recent formulation of VTST was applied,[21] in which not only the location of the transition state but also the form of the reaction coordinate are chosen variationally as a function of energy and angular momentum. The variations of the transition state and of the reaction coordinate were governed by an ion–neutral interaction potential consisting of the long-range ion–induced-dipole (Langevin) term and the ion–permanent-dipole term. The use of this long-range potential naturally led to a transition state of loose "phase-space theory" character, which seemed quite realistic for this ion–neutral complex. The state-density calculations for this potential were made with a classical VTST phase-space integration approach.[22] An important feature of this approach for application to such a large system as the present one is the separation of the degrees of freedom into conserved modes, treated by relatively fast quantum state-counting methods, and a small group of transitional modes which are treated with the time-consuming but accurate classical phase-space integration tools. A fuller description of the details of this theoretical approach to radiative association kinetics and its application to several radiative-association reactions is being published separately.[23] We refer to this for discussion of such important but complex questions as the importance of short-range potential terms in the NO^+/pentanone system and the comparison of the VTST approach with trajectory methods.

It is a noteworthy prediction of statistical theory[1,23] that in the low-efficiency limit, where only a small fraction of ion–neutral collisions result in stabilized complexes, k_{ra} becomes independent of the nature of the transition state, depending only on partition functions for the reactants and for the complex. Thus the nature of the interaction potential between ion and neutral drops out of the theory. The present experiments approach but do not reach the low-efficiency limit, which appears from limited modeling trials to be assured only for efficiencies below perhaps 10^{-3}, compared with the present efficiencies of $2-8 \times 10^{-2}$. However, the efficiencies here are low enough that we expect rather low sensitivity to the details of the assumed form of the potential. For instance, complete neglect of the strong ion–permanent-dipole term would raise our estimate of the binding energy by only 1.5 kcal mol^{-1}.

This particular ion–neutral system has the complication that the charge transfer from NO^+ to pentanone is only slightly endothermic (1.2 kcal mol^{-1} based on the reported IE of 9.31 eV for 3-pentanone),[24] and provides an additional exit channel for the metastable complex. The charge-transfer channel was included in the VTST calculations as a competitive transition state, assuming (as may or may not be valid) that all charge-transfer reactions proceed through the metastable complex. Within this treatment, it was found that the charge-transfer rate was best reproduced assuming a charge-transfer endothermicity of 0.2 kcal mol^{-1}. The observed weak temperature dependence was actually best modeled using an endothermicity of 1.5 kcal mol^{-1}, but this gave a rate too low by a factor of about 5. The inclusion of the charge-transfer channel in the modeling has only a small effect on the modeling of the association process. Complete neglect of the charge-transfer channel changes the assignment of the binding energy based on k_{ra} by only 0.4 kcal mol^{-1}. This mutual near-independence of the charge-transfer and association processes in the kinetic model can be partially rationalized on the basis that it is those metastable complexes with the smallest internal energy that contribute most heavily to the association process, whereas those with substantial excess internal energy contribute most heavily to the endothermic charge transfer. Thus these two processes are to a certain degree not in actual kinetic competition.

(c) Ab Initio Calculations. The kinetic modeling requires vibrational frequencies and infrared intensities for the normal modes of the complex. Recent studies of rates of both radiative association[25] and radiative cooling[26] have encouraged us to think that Hartree–Fock level calculations with a modest basis set can give these quantities with sufficient accuracy for radiative association modeling, since the modeling is not strongly sensitive to variations in these parameters. The present results were computed using the GAUSSIAN program suite[27] at the HF/6-31G* level. A true minimum on the potential surface was found with the NO^+ bound to the ketone with the expected long bond between the nitrogen and the carbonyl oxygen, and the following structural features: NO coplanar with the C–C(O)–C

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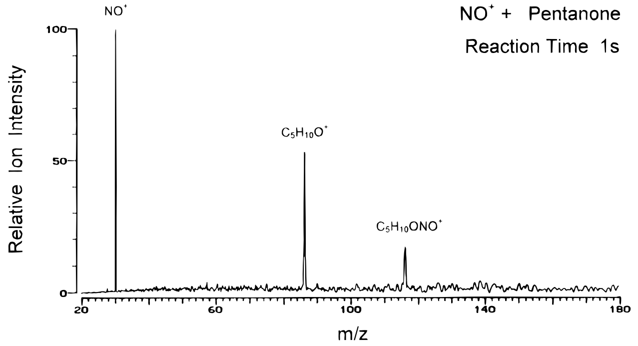

Figure 1. Illustrative spectrum of NO$^+$ (3.2 × 10^{-8} Torr) + $C_5H_{10}O$ (7 × 10^{-9} Torr) with a reaction time of 1 s at room temperature.

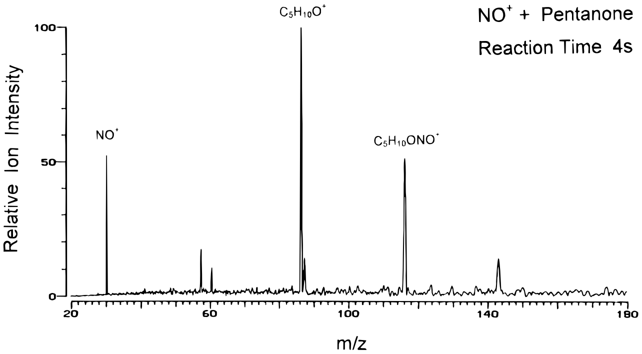

Figure 2. Illustrative spectrum of NO$^+$ (3.2 × 10^{-8} Torr) + $C_5H_{10}O$ (7 × 10^{-9} Torr) with a reaction time of 4 s at room temperature.

framework of the ketone; *d*(N to carbonyl oxygen) = 2.18 Å, ∠COH = 148.8°, ∠ONO = 97.1°. However, this level of theory is not expected to be very reliable for the long N···O bond, or for the normal mode frequencies associated with this bond. Trials at the higher MP2/6-31G* level were made for model systems of NO$^+$ binding to formaldehyde, methanol, and acetone, and the results suggested that a bond length shorter by 0.2 Å would be a better estimate, along with a reduction by a factor of 1.4 in the frequencies of the five transitional modes. Thus a *d*(N to carbonyl) bond length of 1.98 Å was assigned as the best estimate. The Hartree–Fock frequencies and IR intensities for the complex from the calculations are given in Table 1. The Hartree–Fock frequencies given in Table 1 were all scaled down by a factor of 0.89 for use in the kinetic modeling to correct for a well-known systematic bias at this level of *ab initio* theory.

Experimental Section

The instrument and techniques have been described in detail elsewhere.[8,15] The Fourier-transform ion cyclotron resonance (FT-ICR) spectrometer has a 2.54-cm cubical cell in a 1.4-T electromagnet. Electron impact ionization was used (nominal electron energy 15 eV). Following the ionization pulse and cooling time, the parent ion of pentanone and any other ion species besides NO$^+$ were ejected by single-frequency and swept-frequency ejection pulses. Then a reaction period varying from 100 ms to 10 s, depending on pressure, was provided for the reactions to proceed. After that the extent of association and charge transfer was determined by the FT-ICR detection sequence. A time plot of reaction extent versus reaction time was acquired for each reaction at each pressure, followed by the derivation of the association and charge-transfer reaction rates from the reactant and product curves. Figures 1 and 2 show illustrative spectra.

The electron impact ionization technique used in this work produces ions with excess internal energy, in addition to the initial kinetic energy acquired by those ions formed near the edge of the cell. However, for correct measuring of radiative association rates it is important to have the reacting ions thermalized, which can be accomplished by collisions with neutrals. Accordingly a cooling period was provided following the series of ejection pulses removing all ionic species other than NO$^+$. After this cooling period, another series of ejection pulses again removed all ions other than NO$^+$, following which the reaction processes were followed.

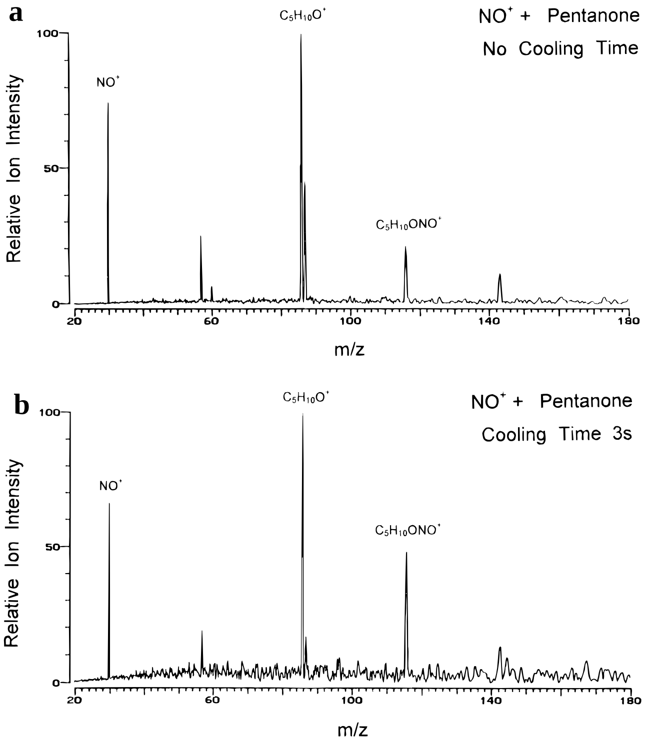

Figure 3. Spectra of NO$^+$ (3.2 × 10^{-8} Torr) + $C_5H_{10}O$ (7 × 10^{-9} Torr) with a reaction time of 3 s at 305 K, showing the effect of cooling of the reactants: (a) no cooling time; (b) cooling time of 3 s.

Figure 3a shows a spectrum obtained with no cooling time. It is seen that under these conditions about 90% of NO$^+$ reactions gave charge-transfer-derived products (*m/z* 86, 57, 87, and 143) while only 10% formed the association adduct (*m/z* 116). The spectrum in Figure 3b was acquired with a 3-s cooling time, corresponding to 5–6 NO$^+$ collisions with neutrals prior to the reaction. For these conditions charge transfer was only 3 times faster than association.

It was found that further increase of cooling time, or addition of a bath gas (SF_6) in the cell (up to 30 collisions prior to the reaction), did not change the charge-transfer-to-association ratio substantially. This indicates that 5 collisions, along with radiative cooling for 3 s, sufficed for removal of all significant superthermal internal and kinetic energy from NO$^+$. Accordingly, at all pressures used, a sufficient cooling period was provided to give at least 5 collisions of NO$^+$ with neutral pentanone.

The NO pressure used was 3.2 × 10^{-8} Torr while the pentanone pressure varied from 3 × 10^{-9} to 1.3 × 10^{-7} Torr. Pressure was read from the ionization gauge and calibrated using the known value[28] of the bimolecular rate constant of proton transfer from methane molecular ion to methane ($k = 1.14 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1}) along with standard gauge correction factors.[29] Instrument control, detection, and data processing used the IonSpec data system. The experimental sequence was repeated for several different temperatures ranging from 300 to 400 K. Temperature was measured from a copper–constantan thermocouple attached to one of the trapping plates. Details of the heating and temperature measurement arrangements in this instrument have been described.[30]

Results

The kinetic scheme (eqs 2–4) was confirmed by double resonance experiments. The association adduct (*m/z* = 116),

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once formed, did not react any further. The kinetic scheme would be more complicated if reactions between $C_5H_{10}O^+$ and NO neutral, either charge transfer or association, occurred with significant rates. To exclude these possibilities we ran an experiment with continuous ejection of $C_5H_{10}O^+$ ($m/z = 86$). The ejection did not have any effect on the intensities of NO^+ ($m/z = 30$) or $C_5H_{10}O^+$ ($m/z = 116$). This shows that under the conditions of these experiments the contributions of reverse charge transfer or reverse association were negligible. However, increasing the NO pressure up to 1.0×10^{-6} Torr allowed us to observe the charge transfer from $C_5H_{10}O^+$ to NO neutral proceeding with a rate constant some 10 times lower than that for reaction 3.

It may seem surprising that the nearly thermoneutral charge-transfer reaction 3 is negligibly slow in the reverse direction, in contrast to its substantial rate in the forward direction. This observation can be rationalized by comparing the orbiting rate constants in the two directions. The value for reaction 3 with a dipole correction[18] is 3.2×10^{-9} cm^3 molecule^{-1} s^{-1} whereas the value for the reverse reaction is only 0.82×10^{-9} cm^3 molecule^{-1} s^{-1}. Given this difference and the fact that under the experimental conditions the NO pressure is low relative to the ketone pressure, the reverse charge transfer is not expected to be observed. However, one would expect to see the reverse charge transfer at higher NO pressures, as was observed.

Surprisingly, no association between $C_5H_{10}O^+$ and NO was observed even at high NO pressures, which cannot be explained only by the difference in the orbiting rates. However, an additional factor which can account for this result is that association from the $C_5H_{10}O^+$ direction competes with reverse charge transfer, which is an *exothermic* reaction. It is well-known in general that association is substantially suppressed by the presence of an exothermic exit channel.[9] The quantitative modeling in this case confirms that even 1 or 2 kcal of exothermicity for the reverse charge transfer would be expected to reduce the association probability by a major factor.

Figure 1 shows a typical spectrum for reaction of NO^+ with pentanone. For these reaction conditions and this temperature, it is seen that less than a half of the NO^+ has reacted to give the products, and that the charge transfer proceeds approximately three times faster than formation of the association adduct. At longer reaction times the products of slower processes begin to appear (Figure 2). As was proved by double-resonance experiments, ions with m/z 57, 87, and 143 come from reactions of pentanone parent ion $C_5H_{10}O^+$ ($m/z = 86$):

$$C_5H_{10}O^+ \ (86) \rightarrow C_3H_5O^+ \ (57) + C_2H_5 \qquad (9)$$

$$C_5H_{10}O^+ \ (86) + C_5H_{10}O \rightarrow C_5H_{11}O^+ \ (87) + C_5H_9O \qquad (10)$$

$$\rightarrow C_8H_{15}O^+ \ (143) + C_2H_5 \qquad (11)$$

Since these ions do not interfere in processes 2−4 their intensities can be combined and added to the intensity of the parent ion. This sum will therefore represent an intensity of the charge transfer channel 3 without any complications to the kinetic scheme. Indeed, from Figure 2, comparison of the charge-transfer (ions with m/z 86, 57, 87, and 143) and the association (m/z 116) product intensities gives a ratio of 3, which is the same as from Figure 1, showing that the charge-transfer/association branching ratio is constant as the ion population evolves in time.

An illustrative time plot is shown in Figure 4. The overall rate constant for NO^+ disappearance, k_{rx} (the sum of the association and the charge-transfer rate constants), was obtained for each individual pressure. After that, knowing the ratio of the charge transfer and the association rates, the individual bimolecular rate constants for both channels were easily obtained. Observation of the pressure dependence in each case (see Figure 5 for example) showed no significant dependence of the association rate constant at pressures up to $(1-2) \times 10^{-7}$ Torr of pentanone. This showed definitively that there was no significant contribution from three-body (collisional) association in the measurements of k_{ra} reported in Table 2. Since no pressure dependence was found, no value can be given for the collisional association rate constant, but we can say that the transition pressure (at which radiative and collisional association rates are equal; see ref 3) is greater than about 1×10^{-6} Torr.

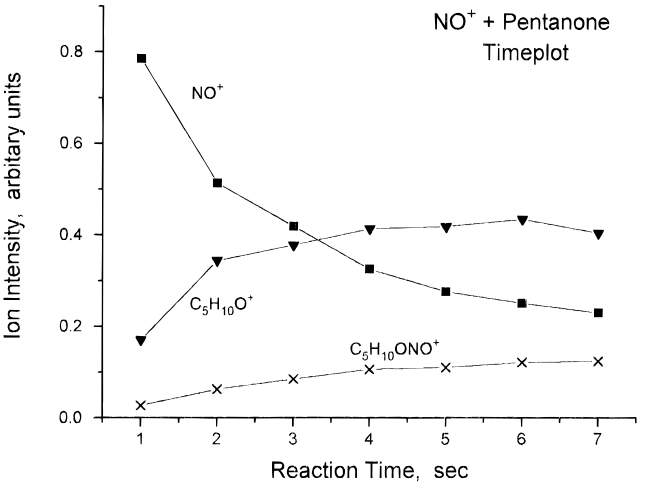

Figure 4. Time plot of the species NO^+ (squares), $C_5H_{10}O^+$ (triangles), and $C_5H_{10}ONO^+$ (crosses). Pressure(NO) = 3.2×10^{-8} Torr, Pressure($C_5H_{10}O$) = 3×10^{-9} Torr, $T = 330$ K.

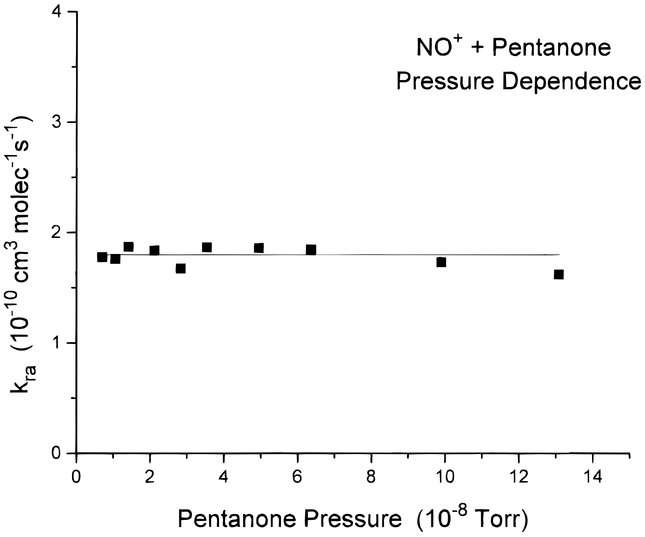

Figure 5. The radiative association rate constant k_{ra} as a function of pentanone pressure at 305 K.

The experimental data are given in Table 2. As expected, the radiative association is fairly fast at room temperature (collisional efficiency of radiative stabilization about 6%). As temperature goes up the association rate drops rapidly; at 400 K it is so low that we can only set an upper limit on k_{ra}. The charge transfer is quite efficient (about 25% of the collisional rate) in this temperature range.

Binding Energy. (a) Binding Energy Estimate from Ion−Molecule Equilibrium Results. Reents and Freiser[14] reported the binding energy of this complex as 2.09 eV. However, the kinetic analysis of our radiative association data was in strong

Table 2. Temperature Dependence of NO^+ Association with 3-Pentanone (Experimental Results)

T (K)	$k_{rx}{}^a$	$k_{ct}{}^{a,b}$	$k_{ra}{}^a$	Φ^c
305	6.40	4.60	1.80	0.056
320	6.30	4.82	1.48	0.046
330	6.16	4.78	1.38	0.043
336	6.65	5.65	1.00	0.031
345	6.75	5.79	0.96	0.030
358	7.39	6.64	0.75	0.023
370	8.15	7.50	0.65	0.020
385	8.08	7.59	0.49	0.015
400	8.80	8.57	≤0.23	≤0.007

[a] 10^{-10} cm^3 molecule^{-1} s^{-1}. [b] Bimolecular rate constant for charge transfer reaction (eq 3). [c] Collisional efficiency of radiative association k_{ra}/k_{orb} taking the orbiting rate constant to be 3.2×10^{-9} cm^3 molecule^{-1} s^{-1} (ref 18).

disagreement with this value; on reexamination of their analysis it was realized that their NO^+ affinity scale was anchored to an old and erroneous proton affinity scale. It is thus appropriate first to reassess their equilibrium results and correct their binding energy assignments for comparison with the present results.

The addition of NO^+ to a hydrogen-containing molecule can be written

$$RH + NO^+ \rightarrow RHNO^+ \qquad (12)$$

The negative enthalpy of this reaction is the NO^+ affinity, NOA, of the molecule RH. Usually the only unknown heat of formation among the species in eq 12 is the heat of formation of $RNOH^+$, which can be obtained from the proton affinity of RNO. Thus for those cases where the proton affinity of RNO is independently known, the NOA can be derived independently, and can be used to anchor the NOA scale from equilibrium measurements like those of Reents and Freiser. Reents and Freiser anchored their NOA scale using the proton affinity of C_2H_5ONO from high-pressure mass spectrometer work, but used an obsolete proton affinity scale. Their scale can be anchored to currently accepted thermochemistry using the accepted proton affinities[31] of either CH_3ONO or C_2H_5ONO, and it seems sensible to give equal weight to these two anchor values. Making this analysis using accepted values gives the NOA of CH_3OH as 29.9 kcal mol^{-1} and the NOA of C_2H_5OH as 35.9 kcal mol^{-1}. Comparing these values with Table II of ref 14 and taking the average of the two corrections, it is seen that the NOA scale of Reents and Freiser should be lowered by 5.4 ± 1.0 kcal mol^{-1} (0.23 eV). The NOA of 3-pentanone should thus be corrected to 42.7 kcal mol^{-1} (1.85 eV) with an uncertainty of perhaps 2−3 kcal mol^{-1}. This is best regarded as an enthalpy of dissociation at 300 K, but calculation of the thermal correction using the present *ab initio* vibrational frequencies of the complex indicates that the correction to 0 K gives an insignificant change, so this same value can be taken as the dissociation energy D_o.

(b) Binding Energy Estimate from k_{ra}. In order to estimate the binding energy from the present radiative association data, it is necessary to calculate the expected k_{ra} as a function of the assumed binding energy and compare the calculated values with experiment. The calculations were carried out as described above.

As an illustration, the final results of the k_{ra} calculation at a temperature of 350 K are displayed in Figure 6 as a function of assumed binding energy. Also marked on the figure is the experimental 350 K value of $k_{ra} = 0.86 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} (assigned by smoothing and interpolating the points shown in Figure 7). It is seen from the figure that this observed k_{ra} value corresponds to a binding energy of 1.76 eV (40.5 kcal mol^{-1}), with an error range of ±0.10 eV corresponding to a rate uncertainty of a factor of 2.

Table 3. Comparison of Observed Radiative Association and Charge Transfer Kinetics with VTST Predictions for a Complex Binding Energy of 40.5 kcal mol^{-1} [a]

T (K)	$k_{ra}(\text{expt})^b$	$k_{ra}(\text{theory})^b$	$k_{ct}(\text{expt})^{b,c}$	$k_{ct}(\text{theory})^{b,c}$
305	1.80	1.85	4.60	5.03
320	1.48	1.41	4.82	5.17
330	1.38	1.17	4.78	5.25
336	1.00	1.05	5.65	5.28
345	0.96	0.90	5.79	5.34
358	0.75	0.70	6.64	5.40
370	0.65	0.56	7.50	5.45
385	0.49	0.43	7.59	5.47
400	≤0.23	0.32	8.57	5.46

[a] For comparison, note that the collision rate constant[18] for formation of metastable complexes is about 32×10^{-10} cm^3 molec^{-1} s^{-1}. [b] 10^{-10} cm^3 molecule^{-1} s^{-1}. [c] Theoretical charge transfer modeling assumed a charge transfer endothermicity of 0.2 kcal mol^{-1}.

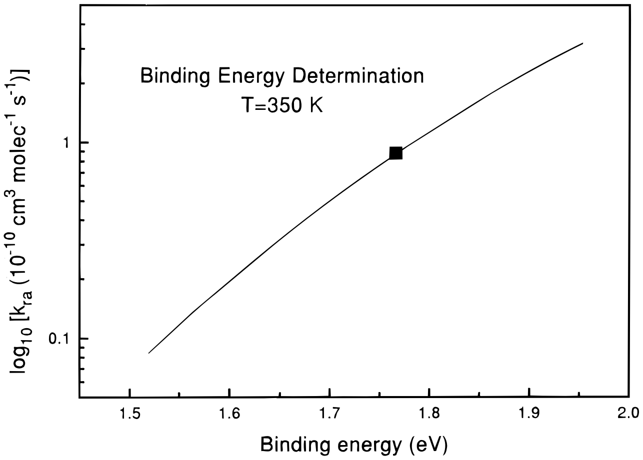

Figure 6. Fit of the experimentally observed radiative association rate constant (square) to VTST kinetic modeling to estimate the dissociation energy of the NO^+/pentanone complex.

(c) Final Binding Energy Assignment. For assessing the absolute binding energy of this complex, there seems no reason to prefer either of the results given above. They are each expected to have good absolute reliability, and each is probably uncertain to one or two tenths of an electronvolt. Fortunately they agree well, and it seems realistic to make a final assignment of 1.80 ± 0.1 eV (41.6 ± 2 kcal mol^{-1}) for the 0 K binding energy of this complex.

Discussion

The comparison of the experimental results for the radiative association with the modeling predictions is shown as a function of T in Figure 7a. The slope of the VTST temperature plot fits the experimental points essentially perfectly. The simple RRKM/standard hydrocarbon model is less accurate in reproducing the observed temperature dependence. It gives the temperature dependence qualitatively correctly, but this approach predicts a noticeably faster falloff in rate with increasing temperature than is actually observed.

Lin[5] suggested that the simple RRKM-based theory of ref 8 predicted a nearly linear plot of log k_{ra} versus T, and showed that several reactions do actually give such linear plots. To follow this idea, the temperature-dependence comparisons of Figure 7a are replotted in Figure 7b using log k_{ra} coordinates. Indeed, it is seen that over this temperature range, the

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(31) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

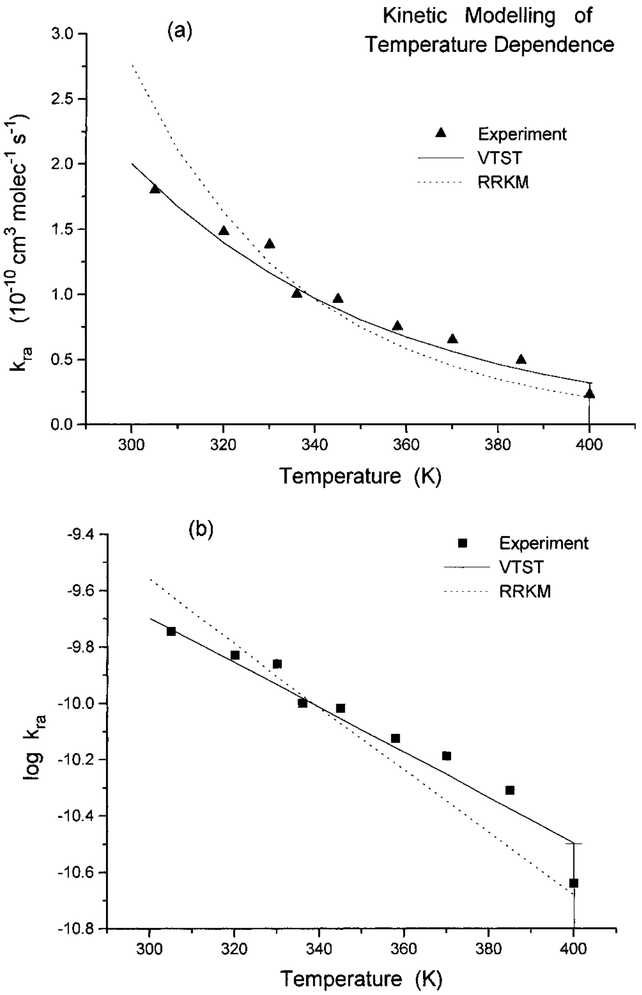

Figure 7. Temperature dependence of k_{ra} in normal (a) and semilogarithmic (b) coordinates. Triangles represent experimental results, solid lines show VTST calculations, dashed lines show RRKM modeling.

experimental points as well as both theoretical approaches give accurately linear log k_{ra} vs T behavior. As will be discussed in detail,[23] the detailed VTST theory confirms that this functional form holds to a good approximation at temperatures sufficiently high that the vibrational energy content of the reactants dominates over their translational and rotational energies, which is true at room temperature and above for systems of this size. A plot of ln(k_{ra}) vs $1/T$ is also linear to more or less the same degree of accuracy for the present data over this limited temperature range, as was noted by Lin[5] to be true for the systems he reported.

The charge-transfer rate constant (eq 3) was found to increase slightly with temperature, as is reasonable for such a slightly endothermic reaction. It is not known whether the charge-transfer channel proceeds from the metastable collision complex in competition with redissociation (as was assumed in the modeling in this paper), or alternatively via a long-range charge-transfer process not involving formation of a long-lived metastable complex.

The perfect agreement of the VTST calculation with the observed temperature dependence gives encouragement to thinking that this level of theoretical sophistication gives a good description of the kinetics, at least near the low-efficiency regime. Future work will investigate the role of the (presently neglected) short-range terms in the potential, but it is expected that these will principally affect the high-efficiency regime, which will only be accessed for the NO^+/pentanone system at substantially lower temperatures than used here. The absolute association rate is reproduced within satisfactory error limits by the VTST calculation using Reents and Freiser's[14] (corrected) D_0 value. This is gratifying, but perhaps not very telling, since we consider the uncertainty in D_0 to be substantial, and we feel justified in considering the D_0 value obtained by fitting the present results to be of similar quality to that of Reents and Freiser.

The generic RRKM calculation, combined with the estimate of IR radiative rates from the "standard hydrocarbon" model,[8] gives agreement with the observed absolute k_{ra} values if the binding energy is taken to be 1.75 eV, which is in satisfactory (and certainly somewhat fortuitous) agreement with our best assigned value. A generic "standard hydrocarbon" estimate (which is essentially similar to the RRKM estimate reported here) for 300 K can also be taken directly from Figure 1 of ref 8, and gives similar agreement with the experiment assuming a binding energy of about 1.8 eV. Agreement of experiment with these low-level theoretical estimates has no profound significance, but does give support to the validity and usefulness of the generic estimation approach to predicting approximate numerical values for radiative association kinetics without the effort of detailed *ab initio* and statistical computations.

Conclusions

The VTST model of association/dissociation leads to an accurate quantitative description of the temperature dependence, which indicates a satisfactory fundamental understanding of this aspect of the kinetics. The simple RRKM analysis was less accurate in reproducing the exact slope of the observed temperature dependence. In accord with observations for other systems, the temperature dependence of k_{ra} was linear when plotted as ln(k_{ra}) vs T. This is not particularly significant or surprising for data over this relatively small temperature range. The inherent significance of the slopes of these plots is not yet clear, and will be the subject of future work.

The VTST calculation with *ab initio* radiative intensities gives the absolute value of k_{ra} within a factor of 2 of the experimental value if the binding energy of Reents and Freiser is assumed. However, we place confidence in the independent binding energy assignment based on the fit of this theory to the present experimental results, and consider the resulting new value for the binding energy value to have reliability comparable to that of Reents and Freiser. Accordingly we use it to propose a new and presumably more reliable best value of 1.80 ± 0.10 eV for the binding energy of this complex.

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