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Determination of ionization energies by the thermokinetic method

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Abstract

Charge transfer reactions of the type $M^{\cdot+}+B \rightarrow B^{\cdot+}+M$ have been studied in order to test the applicability of the "thermokinetic" method to the determination of ionization energies (IEs). Three examples are presented with M=benzene, cyclopentanone, and vinyl alcohol. The correlation observed between the bimolecular rate constants and IE(B) allows the determination of IE(M) with a mean deviation of ~0.02 eV with respect to spectroscopic values. One other advantage of the method is to provide ionization energies of unstable neutrals. The role of various corrective terms, and of possible geometry changes during charge transfer reactions are discussed. (Int J Mass Spectrom 210/211 (2001) 189–201) © 2001 Elsevier Science B.V.

Keywords: Ionization energy; Thermokinetic method; Benzene; Cyclopentanone; Vinyl alcohol

1. Introduction

Most of the experimental techniques for determination of ionization energies (ionization thresholds, ion/molecule equilibria) [1] require the presence of the corresponding neutral species during the experiments. It is known however that stable ions exist which are not associated with stable neutrals but with species that may spontaneously rearrange or even dissociates. This is obviously the case of free radicals [2], carbenes [3], neutralized distonic ions [4] but also of more conventional structures such as, for example imines or enols [5]. The new experimental method of determination of ionization energies described in the present work is intended to apply, inter alia, to this large body of target compounds. It is based on the measurement of the rate constant, k_{exp}, for bimolecular electron transfer reactions between the ion of interest M^+ and a series of reference neutrals B

$$M^+ + B \overset{k_{exp}}{\rightarrow} M + B^+ \qquad (1a)$$

By analogy with the thermokinetic method developed for proton transfer reactions [6,7], the reaction efficiency R of the electron transfer reaction (1a) ($R=k_{exp}/k_{coll}$, where k_{coll} is the calculated collision

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rate) may be correlated with the corresponding Gibbs energy change $\Delta_1 G°$ and consequently to the ionization energy difference IE(B)−IE(M). By measuring k_{exp} for a series of compounds B of known ionization energies it is thus possible to deduce the ionization energy of the specie M. In this article we examine the applicability of this "thermokinetic" correlation between k_{exp} and the difference IE(B)−IE(M) by considering several test cases.

2. Experimental

All reactions were monitored in a Bruker-CMS-47 Fourier transform ion cyclotron resonance (FTICR) mass spectrometer equipped with an external ion source [8]. Experiments consist of transferring all the ions resulting from electron ionization of the precursor of M^+ to the reaction cell located inside the 4.7 T superconducting magnet. The ion M^+ are then selected by ejection of unwanted ionic species by a combination of soft and chirp rf pulses. After selection, the reactant ions are relaxed to thermal energy by introducing argon inside the reaction cell and by imposing a suitable relaxation delay (typically 2 s). Next, the ions were allowed to react for a variable time with neutral B at a pressure in the range 10^{-8} to 10^{-7} mbar. The bimolecular rate constants k_{exp} were deduced from the slope of the logarithmic plot of reactant ions versus reaction time. The estimated error on the experimental rate constant values is $\sim \pm 20\%$.

The collision rate constants, k_{coll} were calculated using either the average dipole orientation (ADO) theory [9a] or the trajectory calculations based on the variational transition state theory (VTST) developed by Su and Chesnavich [9b]. The curve fitting procedure utilized to correlate reaction efficiencies and ionization energies uses a nonlinear iterative least square procedure implemented in the IGOR PRO 3.1 package (Wavemetrics Inc., Lake Oswego, OR, 1996). The numerical values of the fitting parameters given in the text are the average of the results obtained using either the ADO or the VTST methods in the calculation of k_{coll}. It is observed that both methods give comparable results and that no significant uncertainty is attached with the mean used for estimating reaction efficiency.

3. Method

For a nonresonant charge transfer process occurring at low velocity of the reactants, where the ion trajectory is significantly affected by the polarizability and the dipole moment of the molecule, the reaction may be considered as a possible exit channel of a ion–molecule intermediate complex. This point of view seems corroborated by the observation that, in most cases, the reaction rate of charge transfer is close to the theoretical capture collision limit [1d]. Moreover, it has been demonstrated that the measurement of the equilibrium constant for charge transfer reactions allows the determination of ionization energies [10]. We can thus confidently consider that a thermokinetic method, based on the formation and dissociation of an intermediate collision complex, may provide such thermochemical information.

Let us consider that the charge exchange reaction (1a) involves the intermediacy of a charge transfer complex, $[MB]^+$, which may be formed either from the couple M^++B, with a collision rate k_{1c} or from M+B^+, at the collision rate k_{2c} and may readily dissociate with unimolecular rates k_{-1} and k_{-2}:

$$M^+ + B \underset{k_{-1}}{\overset{k_{1c}}{\rightleftharpoons}} [MB]^+ \underset{k_{2c}}{\overset{k_{-2}}{\rightleftharpoons}} M + B^+ \tag{1b}$$

Assuming that the steady state approximation can be applied to $[MB]^+$, the experimental bimolecular rate constant for reaction (1a) in the forward and in the backward directions, k_f and k_b, can be expressed by

$$k_f = k_{1c} /[1 + (k_{-1}/k_{-2})] \tag{2}$$

and

$$k_b = k_{2c} /[1 + (k_{-2}/k_{-1})] \tag{3}$$

There are several means to express the ratio of dissociation rates (k_{-1}/k_{-2}) using either the canonical (fixed T) or the microcanonical (fixed E) thermochemical formalisms [9c]. Using the canonical expression of the rate constants k_{-1} and k_{-2} the ratio is given by

$$(k_{-1}/k_{-2}) \;=\; \exp(\Delta_1 G^{\circ\ddagger}/RT) \tag{4}$$

where $\Delta_1 G^{\circ\ddagger}$ is the difference in Gibbs energy between the two transition structures leading to M+B$^+$ and M$^+$+B, respectively. As already done for proton transfer reactions [6], $\Delta_1 G^{\circ\ddagger}$ may be expressed as a function of the Gibbs energy change $\Delta_1 G^\circ$ for reaction (1a) by introducing an "apparent energy barrier," $\Delta G^\circ{}_a$, thus giving

$$(k_{-1}/k_{-2}) = \exp[(\Delta_1 G^\circ + \Delta G^\circ_a)/RT] \tag{5}$$

and consequently

$$k_f = k_{1c}/[1 + \exp[(\Delta_1 G^\circ + \Delta G^\circ_a)/RT]] \tag{6}$$

and

$$k_b = k_{2c}/[1 + \exp[-(\Delta_1 G^\circ + \Delta G^\circ_a)/RT)]] \tag{7}$$

Another approach consists in expressing the equilibrium constant K of reaction (1a) in terms of the forward and backward reaction rates. The so-called "detailed balancing" principle leads to the equality:

$$K = k_f/k_b \tag{8a}$$

if both reaction rates are determined under conditions of thermal equilibrium of the reactants. When using expressions (2) and (3) to express k_f and k_b, this equality becomes

$$K = k_{1c}\,k_{-2}/k_{2c}\,k_{-1} \tag{8b}$$

The ratio of the unimolecular dissociation rates is consequently given by

$$(k_{-1}/k_{-2}) = (k_{1c}/k_{2c})K = (k_{1c}/k_{2c})\exp(\Delta_1 G^\circ/RT) \tag{9}$$

and the forward and backward rates by

$$k_f = k_{1c}/[1 + (k_{1c}/k_{2c})\exp(\Delta_1 G^\circ/RT)] \tag{10}$$

and

$$k_b = k_{2c}/[1 + (k_{2c}/k_{1c})\exp(-\Delta_1 G^\circ/RT)] \tag{11}$$

Note that, comparing the two means to express k_{-1}/k_{-2} [Eqs. (5) and (9)] it appears that ΔG°_a is equal to

$$\Delta G^\circ_a = RT\ln(k_{1c}/k_{2c}) \tag{12}$$

In the present investigation we will make use of Eqs. (6) [or Eq. (7)] and (10) [or Eq. (11)] in an attempt to deduce the Gibbs energy change of the charge transfer process and, further, to determine ionization energies. The use of $\Delta_1 G^\circ = \Delta_1 H^\circ - T\Delta_1 S^\circ$ necessitates to examine the relationship between the enthalpic term $\Delta_1 H^\circ$ and the ionization energies of M and B, and to consider the entropic terms $\Delta_1 S^\circ$ associated with the charge transfer in reaction (1a).

It should be recalled that ionization energies are generally determined by photoionization techniques and, in most of the cases, the tabulated values are adiabatic ionization energies i.e. the difference in the heats of formation of the ion and the molecule at 0 K. At a given temperature T, the enthalpy difference $\Delta_1 H^\circ$ is not rigorously equal to the adiabatic ionization energy difference IE(B)−IE(M). A corrective term, taking into account the possible difference in heats capacities of the molecules and the corresponding ions, must be introduced:

$$\Delta_T H^\circ = \int [C_p(B^+) - C_p(B)]dT - \int [C_p(M^+) - C_p(M)]dT \tag{13}$$

and consequently:

$$\Delta_1 H^\circ = IE(B) - IE(M) + \Delta_T H^\circ \tag{14}$$

For a pure charge transfer process, it is expected that the structure of the ion does not fundamentally differ from that of the molecule. Consequently, the various contributions to C_p should cancel and the term $\Delta_T H^\circ$ may be neglected. However, appreciable participation to $\Delta_T H^\circ$ may originate from the electronic and vibra-

Table 1
Parameters relevant to the "forward" charge transfer reactions: $[\text{benzene}]^{\cdot+}$ + B → benzene + $[\text{B}]^{\cdot+}$.

B	IE(B)[a] (eV)	μ[b] (D)	α[c] ($Å^3$)	$k_{\exp(f)}$ ($\times 10^{10}$) ($cm^3\ mol^{-1}\ s^{-1}$)	$k_{\mathrm{coll}(f)}$ ($\times 10^{10}$)[d] ($cm^3\ mol^{-1}\ s^{-1}$)	$R_{(f)}$[e] (%)
Propylbenzene	8.72	0.6	16.0	9.5	13.9 (14.7)	92 (97)
Bromobenzene	8.98	1.7	14.7	10.8	15.6 (17.1)	93 (94)
Chlorobenzene	9.07	1.7	14.1	12.2	16.4 (18.0)	100
1,4-Difluorobenzene	9.16	0	10.2	6.50	11.0	80 (88)
Fluorobenzene	9.20	1.6	10.3	7.17	15.0 (16.7)	65 (64)
1,2-Difluorobenzene	9.29	(2.8)	10.2	0.32	19.0 (22.8)	2 (2)
1,3-Difluorobenzene	9.33	1.6	10.2	0.14	14.4 (16.0)	1 (1)
1,2,3,4-Tetrafluorobenzene	9.57	(2.8)	10.0	0	18.5 (21.6)	0

[a] Ionization energies, from the compilation by Lias et al. [1b, c].
[b] Dipole moment in debye, experimental values from [17] (in parentheses, estimated from comparison with homologous compounds).
[c] Polarizabilities in $Å^3$ calculated using the method of Miller [18].
[d] Collision rate constant calculated using the ADO model [9a] and, into parentheses, trajectory calculations [9b].
[e] Normalized reaction efficiency, $R = (k_{\exp}/k_{\mathrm{coll}})/(k_{\exp}/k_{\mathrm{coll}})\mathrm{max}$.

tional contributions to C_p, particularly if the geometries of the molecule and the ion are different.

The second point of concern is the entropy change $\Delta_1 S°$. Generally, no significant change in moments of inertia, symmetry numbers and vibrational frequencies is associated with a charge transfer reaction such as reaction (1a). Moreover, the degeneracy of electronic states are canceling between reactants and products, therefore, in most cases, the entropy change $\Delta_1 S°$ is negligible. Exceptions are however possible if changes in rotational symmetry number, splitting between electronic states, or considerable structural changes occur upon ionization.

Replacing now $\Delta_1 G°$ by its general expression $\mathrm{IE(B)} - \mathrm{IE(M)} + \Delta_T H° - T\Delta_1 S°$, it is expected that the forward and backward reaction rates should correlate with the ionization energies following

$$k_f = k_{1c}/[1 + \exp[(\mathrm{IE}(B) - \mathrm{IE}(M) + \Delta_T H° - T\Delta_1 S° + \Delta G_a^{\circ})/RT]] \quad (15)$$

$$k_b = k_{2c}/[1 + \exp[-(\mathrm{IE}(B) - \mathrm{IE}(M) + \Delta_T H° - T\Delta_1 S° + \Delta G_a^{\circ})/RT)]] \quad (16)$$

The experimental determination of energetic quantities by the "thermokinetic" method lies on the measurement of the bimolecular rate constants of a series of reactions involving the unknown, M, and several reference molecules B. The ionization energy of M can be deduced from such experiments by considering a set of reactions involving different molecules B of known ionization energies.

For this purpose the relationships (15) and (16) can be more properly fitted by the parametric functions

$$R_f = k_f/k_{1c} = a/[1 + \exp(b(\mathrm{IE}(B) - c))] \quad (17)$$

$$R_b = k_b/k_{2c} = a/[1 + \exp(-b(\mathrm{IE}(B) - c))] \quad (18)$$

where R_f and R_b are the normalized reaction efficiencies of the forward and the backward processes, respectively. Parameter a is a normalizing factor, whereas b and c are operational parameters in principle equal to $1/RT$ and $\mathrm{IE(M)} - \Delta_T H° + T\Delta_1 S° - \Delta G°_a$, respectively. During the investigation of proton transfer reactions by the thermokinetic method [6,7], it has been observed that an effective temperature T_{eff} should be defined through $b = 1/RT_{\mathrm{eff}}$. This has been interpreted as a consequence of the fact that the considered system is not really in thermal equilibrium. A second observation was that $\Delta G°_a$ is remarkably close to RT_{eff} and the approximation $\Delta G°_a = 1/b$ has been repeatedly used with success for proton transfer reactions [6,7]. As established previously, the rigorous treatment of the kinetic of reaction (1a) leads to $\Delta G°_a = RT \ln(k_{1c}/k_{2c})$. The applicability of the para-

Table 2
Parameters relevant to the "backward" charge transfer reactions: benzene + $[B]^{\cdot+}$ → $[\text{benzene}]^{\cdot+}$ + B

B	$k_{\exp(b)}$ ($\times10^{10}$) (cm^3 mol^{-1} s^{-1})	$k_{\text{coll}(b)}$ ($\times10^{10}$)^a (cm^3 mol^{-1} s^{-1})	$R_{(b)}$^{b} (%)
Propylbenzene	0	10.93	0
Bromobenzene	0	10.42	0
Chlorobenzene	0.031	11.08	0.4
1,4-Difluorobenzene	1.78	11.04	22
Fluorobenzene	3.78	11.46	46
1,2-Difluorobenzene	7.22	11.04	90
1,3-Difluorobenzene	7.98	11.04	100
1,2,3,4-Tetrafluorobenzene	6.50	10.5	86

[a] Using, for the benzene molecule, $\alpha = 10.3$ Å^3 ([18]).
[b] Normalized reaction efficiency, $R = (k_{\exp}/k_{\text{coll}})/\ (k_{\exp}/k_{\text{coll}})$ max.

metric equations (17) and (18) and the validity of the means to estimate $\Delta G°_a$ have been investigated by considering three series of charge transfer reactions involving three simple molecules: benzene, cyclopentanone, and vinyl alcohol.

4. Results and discussion

4.1. Benzene

The adiabatic ionization energy of the benzene molecule has been determined by high resolution threshold photoelectron spectroscopy and is therefore known with a great precision [IE(benzene)=9.243 78 ±0.000 07 eV) [1c]. The following charge transfer reaction has been conducted in the FTICR apparatus with a series of eight neutrals B:

$$C_6H_6^{+} + B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C_6H_6 + B^{+} \tag{1c}$$

For this system, the reaction rates have been determined for the forward as well as for the backward directions allowing the possibility of determination of IE(benzene) using eq. (8), (17), or (18). The results are presented in Tables 1–3.

For reaction (1c), the terms $\Delta_T H°$ and $\Delta_1 S°$, appearing in $\Delta_1 G° = \text{IE(B)} - \text{IE(M)} + \Delta_T H° - T\Delta_1 S°$, should be considered in detail because symmetry change occurs during ionisation of the benzene molecule. The neutral molecule pertains to the D_{6h} symmetry group ($\sigma = 12$) and its ground electronic state is a singlet. After abstraction of one of the outermost electrons, the resulting ions are distorted by the Jahn-Teller effect and, in fact, a mixture of $^1B_{1g}$

Table 3
Parameters relevant to the equilibrium: $[\text{benzene}]^{\cdot+}$ + B → benzene + $[B]^{\cdot+}$

B	$K = k_{\exp(f)}/k_{\exp(b)}$	$\Delta_1 G°$(^{a}) (eV)	$k_{\text{coll}(f)}/k_{\text{coll}(b)}$
Propylbenzene	. . .	. . .	1.27 (1.34)
Bromobenzene	. . .	. . .	1.50 (1.64)
Chlorobenzene	393.5	−0.15 (9.247)	1.48 (1.62)
1,4-Difluorobenzene	3.7	−0.033 (9.220)	1.0
Fluorobenzene	1.9	−0.016 (9.243)	1.31 (1.46)
1,2-Difluorobenzene	0.044	0.08 (9.237)	1.72 (2.07)
1,3-Difluorobenzene	0.018	0.104 (9.253)	1.30 (1.45)
1,2,3,4-Tetrafluorobenzene	. . .	. . .	1.76 (2.06)

[a] $\Delta_1 G° = -RT \ln K = -0.0257 \ln K$ (in eV); into parentheses IE(benzene) = IE(B) $-\ \Delta_1 G° + \Delta_T H° - T\Delta_1 S°$ (with $\Delta_T H° = -0.0014$ eV and $T\Delta_1 S° = -0.282$ eV, see text).

and $^2B_{2g}$ ions, of D_{2h} symmetry ($\sigma=4$), are produced. The splitting between these two electronic states is equal to 0.036 eV (1 eV=96.4853 kJ/mol) and may be responsible of a non-negligible extra contribution to the heat capacity and entropy [10].

The rotational contribution to $\Delta_1S°$ is simply given by $S°_{rot}(M)-S°_{rot}(M^+)=R\ln 4-R\ln 12=-9.1$ J K^{-1} mol^{-1} if one assume that no symmetry change occurs during ionization of the molecules B. The electronic contribution to $\Delta_1S°$ is zero since the entropy difference associated with the ionization of B ($S°_{elec}(B^+_{doublet})-S°_{elec}(B_{Singlet})=R\ln 2$) is counterbalanced by the difference $S°_{elec}(M)-S°_{elec}(M^+)$. Accordingly, if the splitting between the two doublet states of ionized benzene is neglected a total degeneracy of 4 is associated with M$^+$ ions and 1 for the molecule but an entropy of mixing of $-R\ln 2$ should be also considered and consequently $S°_{elec}(M^+)-S°_{elec}(M)=R\ln 4-R\ln 2$. As a consequence, $\Delta_1S°$ is equal to -9.1 J K^{-1} mol^{-1} and $T\Delta_1S°=-2.7$ kJ/mol, i.e. -0.028 eV at 298 K. This value is close to the experimental value of -3.9 ± 0.6 kJ/mol (-0.040 ± 0.006 eV) determined by Lias and Ausloos [10] for reaction (1a) (B=fluorobenzene, $T=350$ K).

The $\Delta_TH°$ term [Eq. (13)] associated to reaction (1a) is expected to be small since M and B pertain to the same chemical family. The only appreciable participation to Eq. (13) may be offered by the splitting of the electronic states in ionized benzene. The electronic contribution to the heat capacity of the M$^+$ ions in the upper state is given by [10]

$$C_p/R = x^2\exp(-x)/[1+\exp(-x)]^2$$

where $x=\Delta E/RT$ (ΔE=magnitude of the splitting). In the case of the benzene ion the energy difference ΔE is equal to 3.5 kJ/mol, by using this value and integrating C_pdT over the temperature range 0–298 K the contribution to $\Delta_TH°$ is equal to $\Delta_TH°=-0.14$ kJ/mol (-0.0014 eV) a value one order of magnitude less than our experimental error, this confirms that the term $\Delta_TH°$ can be generally neglected.

The determination of the equilibrium constant of reaction (1c) using $K=k_f/k_b$ leads directly to $\Delta_1G°$. The ionization energy of the benzene molecule may then be obtained from $\text{IE(M)}=\text{IE(B)}-\Delta_1G°+\Delta_TH°-T\Delta_1S°$. Combining the previous estimates of $\Delta_TH°$ (-0.0014 eV) and $T\Delta_1S°$ (-0.0282 eV) to the $\Delta_1G°$ deduced from the determination of the equilibrium constant K (Table 3), we obtain a mean value IE(benzene)$=9.24_0\pm0.01_3$ eV, in excellent agreement with the spectroscopic value.

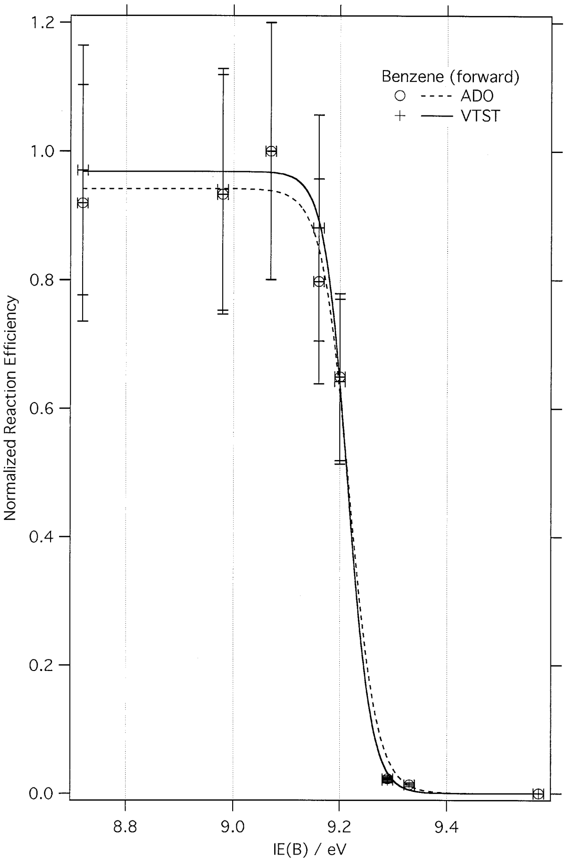

Fig. 1. Normalized reaction efficiencies as a function of IE(B) for the reaction: [benzene]$^{\cdot+}$+B 154 benzene+[B]$^{\cdot+}$.

We turn now to the thermokinetic results. Fig. 1 presents the experimental points of the normalized reaction efficiency of reaction (1c) in the forward direction as a function of IE(B). The continuous line corresponds to a fitting of the experimental data by means of Eq. (17). The fitting parameters a, b, and c are equal to 0.955 ± 0.018; 41.7 ± 6.4 eV^{-1}, and 9.216 ± 0.005 eV, respectively.

Using the relationship $c=\text{IE(M)}-\Delta_TH°+T\Delta_1S°-$

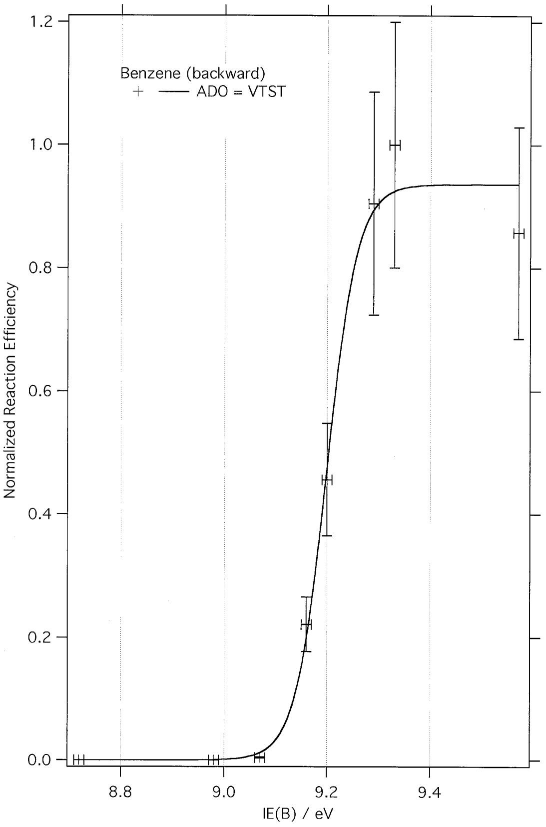

Fig. 2. Normalized reaction efficiencies as a function of IE(B) for the reaction: benzene+[B]$^{\cdot +}$ 154 [benzene]$^{\cdot +}$+B.

$\Delta G°_a$ and, again, $\Delta_T H° = -0.0014$ eV and $T\Delta_1 S° = -0.0282$ eV it follows that IE(M)$=c+\Delta G°_a$ $+0.0268$ eV. We have established that, rigorously, $\Delta G°_a$ is given by $RT\ln(k_{1c}/k_{2c})$ [Eq. (12)]. For reaction (1c) the mean value of the ratio of collision rates is 1.5±0.4 (Table 3) and consequently $\Delta G°_a$ is equal to 0.010±0.005 eV. Combining these data we get IE(benzene)$=9.25_3 \pm 0.00_8$ eV and, using the empirical approximation $\Delta G°_a \approx 1/b$ (0.0240 eV), [IE(benzene)$=9.26_7$ $\pm 0.01_1$ eV] i.e. a value higher by only 1 kJ/mol.

The set of reaction (1c) has been similarly investigated in the backward direction. The results are presented in Table 2 and illustrated by Fig. 2. The fitting parameters are equal to $a = 0.936 \pm 0.035$; $b = 33.6 \pm 8.4$ eV^{-1}, and $c = 9.199 \pm 0.007$ eV. Using again the relationship $c = \text{IE(M)} - \Delta_T H° + T\Delta_1 S° - \Delta G°_a$ and the previously discussed values of $\Delta_T H°$, $T\Delta_1 S°$, and $\Delta G°_a = RT\ln(k_{1c}/k_{2c})$ we obtain IE(benzene)$=9.23_6$ $\pm 0.01_2$ eV. The approximation $\Delta G°_a \approx 1/b$ (0.030 eV) leads to IE(benzene)$=9.25_6 \pm 0.01_8$ eV.

In summary, the estimates of the benzene ionization energy, based on the thermokinetic treatment of reaction (1c) in both directions, fall in a narrow range, 9.24–9.26 eV. A mean value of IE(benzene)$=9.24_4 \pm 0.01_2$ eV is obtained using the expression $RT\ln(k_{1c}/k_{2c})$ to estimate the corrective term $\Delta G°_a$. The value is shifted to $9.26_1 \pm 0.01_8$ eV when using $\Delta G°_a = 1/b$. By comparison with the spectroscopic value, 9.243 78±0.000 07 eV, and owing to the uncertainty ranges, it seems that both means to estimate $\Delta G°_a$ lead to correct results. Concerning the use of $\Delta G°_a = 1/b = RT_{\text{eff}}$ it may be noted that the b values calculated for the forward and the backward reactions are close together and correspond to effective temperatures close to the "room temperature" usually assumed in ICR experiments, i.e. ($T_{\text{eff}} \approx 310$ K).

4.2. Cyclopentanone

The second molecule examined has been chosen to illustrate a case where no $\Delta_T H°$ term and no entropy difference, $\Delta_1 S°$, are expected to be associated with reaction (1a). The adiabatic ionization energy of cyclopentanone has been determined by photoelectron (9.25±0.02 eV [11]; 9.28±0.01 eV [12]) and photoionization (9.26±0.01 eV [13]) experiments, a mean value of 9.263±0.015 eV may be deduced from these experiments [1c].

As for the benzene molecule, the charge transfer reactions between cyclopentanone and a series of reference molecules B have been examined in the forward and in the backward directions

$$\text{cyclopentanone}^{+} + \text{B} \underset{k_b}{\overset{k_f}{\rightleftharpoons}} \text{cyclopentanone} + \text{B}^{+} \qquad (1d)$$

The results are presented in Tables 4–6.

The equilibrium constants of reaction (1d) have been determined from the experimental bimolecular rate constants using the equality $K = k_f/k_b$. Assuming that $\Delta_T H°$ and $\Delta_1 S°$ are negligible, the ionization

Table 4
Parameters relevant to the forward charge transfer reactions: $[\text{cyclopentanone}]^{\cdot+} + \text{B} \rightarrow \text{cyclopentanone} + [\text{B}]^{\cdot+}$

B	IE(B)[a] (eV)	μ[b] (D)	α[c]($Å^3$)	$k_{\exp(f)}$ ($\times 10^{10}$) ($cm^3\ mol^{-1}\ s^{-1}$)	$k_{\text{coll}(f)}$ ($\times 10^{10}$)[d] ($cm^3\ mol^{-1}\ s^{-1}$)	$R_{(f)}$[e] (%)
Bromobenzene	8.98	1.7	14.7	11.1	15.2 (16.7)	95 (96)
Chlorobenzene	9.07	1.7	14.1	12.4	16.0 (17.6)	100
1,4-Difluorobenzene	9.16	0	10.2	6.3	10.8	75 (83)
Fluorobenzene	9.20	1.6	10.3	8.15	14.7 (16.3)	71 (71)
1,2-Difluorobenzene	9.29	(2.8)	10.2	4.4	18.6 (22.3)	31 (29)
1,3-Difluorobenzene	9.33	1.6	10.2	1.6	14.1 (15.7)	14 (14)
1,2,3,4-Tetrafluorobenzene	9.57	(2.8)	10.0	0.3	17.6 (21.1)	2 (2)

[a] Ionization energies, from the compilation by Lias et al. [1b, c].

[b] Dipole moment in debye, experimental values from [17] (in parentheses, estimated from comparison with homologous compounds).

[c] Polarizabilities in $Å^3$ calculated using the method of Miller [18].

[d] Collision rate constant calculated using the ADO model [9a] and, in parentheses, trajectory calculations [9b].

[e] Normalized reaction efficiency, $R = (k_{\exp}/k_{\text{coll}})/(k_{\exp}/k_{\text{coll}})$ max.

energy of the cyclopentanone molecule is simply given by: IE(cyclopentanone)=IE(B)+$RT \ln(K)$. The values reported in Table 6 allow the determination of a mean ionization energy value, IE(cyclopentanone)=$9.26_5 \pm 0.02_4$ eV, in perfect agreement with the mean spectroscopic value recalled previously.

The reaction rate constants associated with reaction (1d) in the forward direction are given in Table 4. The plot of the reaction efficiencies as a function of IE(B) and the corresponding fitting curve are presented in Fig. 3. The fitting parameters a, b, and c of Eq. (17) are equal to 0.985±0.031; 19.7±2.1 eV^{-1} and 9.245±0.007 eV, respectively. Using the relationship IE(M)=$c+\Delta G°_a$ (i.e. considering that $\Delta_T H°$ and $T\Delta_1 S°$ are equal to zero), we obtain IE(cyclopentanone)=$9.23_9 \pm 0.01_3$ eV with $\Delta G°_a$ given by Eq. (12) ($\Delta G°_a = RT \ln(k_{1c}/k_{2c}) = -0.006 \pm 0.005$ eV). When using the approximation $\Delta G°_a \approx 1/b$ (0.051 eV) we derive a slightly higher value, IE(cyclopentanone)=$9.29_6 \pm 0.01_0$ eV.

Comparable results were obtained when considering reaction (1d) in the backward direction. The experimental data given in Table 5 are illustrated in Fig. 4. The values of the fitting parameters where a=1.002±0.019; b=64.8±9.3 eV^{-1}, and c=9.241±0.008 eV. The ionization energy deduced from IE(M)=$c+\Delta G°_a$ is IE(cyclopentanone)=$9.23_5 \pm 0.01_3$ eV with $\Delta G°_a = RT \ln(k_{1c}/k_{2c})$ and IE(cyclopentanone)=$9.25_6 \pm 0.01_1$ eV with $\Delta G°_a = 1/b$ (0.015 eV).

Averaging the ionization energy values obtained by considering reaction (1d) in both directions we obtain IE(cyclopentanone)=$9.23_7 \pm 0.01_3$ eV with $\Delta G°_a = RT \ln(k_{1c}/k_{2c})$ and IE(cyclopentanone)= $9.27_6 \pm 0.01_1$ eV with $\Delta G°_a = 1/b$. Again, the compar-

Table 5
Parameters relevant to the “backward” charge transfer reactions: $\text{cyclopentanone} + [\text{B}]^{\cdot+} \rightarrow [\text{cyclopentanone}]^{\cdot+} + \text{B}$

B	$k_{\exp(b)}$ ($\times 10^{10}$) ($cm^3\ mol^{-1}\ s^{-1}$)	$k_{\text{coll}(b)}$ ($\times 10^{10}$)[a] ($cm^3\ mol^{-1}\ s^{-1}$)	$R_{(b)}$[b] (%)
Bromobenzene	0	17.5 (21.3)	0
Chlorobenzene	0	18.7 (22.7)	0
1,4-Difluorobenzene	0.4	18.6 (22.6)	4 (5)
Fluorobenzene	0.6	19.4 (23.5)	7 (5)
1,2-Difluorobenzene	8.1	18.6 (22.6)	96 (97)
1,3-Difluorobenzene	8.4	18.6 (22.6)	100
1,2,3,4-Tetrafluorobenzene	7.9	17.7 (21.4)	100

[a] Using, for the cyclopentanone molecule, μ = 2.9 D [17] and α = 9.3 $Å^3$ ([18]).

[b] Normalized reaction efficiency, $R = (k_{\exp}/k_{\text{coll}})/(k_{\exp}/k_{\text{coll}})$ max.

Table 6
Parameters relevant to the equilibrium: $[\text{cyclopentanone}]^{\cdot +} + \text{B} \rightarrow \text{cyclopentanone} + [\text{B}]^{\cdot +}$.

B	$K = k_{\exp(f)}/k_{\exp(b)}$	$\Delta_1 G^{\circ a}$ (eV)	$k_{\text{coll}(f)}/k_{\text{coll}(b)}$
Bromobenzene	. . .	. . .	0.87 (0.78)
Chlorobenzene	. . .	. . .	0.86 (0.78)
1,4-Difluorobenzene	15.8	−0.071 (9.231)	0.58 (0.48)
Fluorobenzene	13.6	−0.067 (9.267)	0.76 (0.69)
1,2-Difluorobenzene	0.54	0.016 (9.274)	1.0 (0.99)
1,3-Difluorobenzene	0.19	0.043 (9.287)	0.76 (0.69)
1,2,3,4-Tetrafluorobenzene	. . .	. . .	0.99 (0.99)

[a] $\Delta_1 G^\circ = -RT \ln K = -0.0257 \ln K$ (in eV); in parentheses IE (cyclopentanone) = IE(B) − $\Delta_1 G^\circ$.

ison with the spectroscopic value is correct if we consider the indicated (statistical) uncertainties on the various measurements. Consequently, it seems hard to decide whether ΔG°_a should be estimated using $RT \ln(k_{1c}/k_{2c})$ or $1/b$ since the spectroscopic IE value falls in between the two estimates. It may be observed, however, that very different parameters b are calculated for reaction (1d) in the forward and in the backward direction, the values corresponds to effective temperatures T_{eff} as different as 590 and 180 K. The reasons of this difference is unclear but we note that using an effective temperature T_{eff} of 310 K, as in the case of the benzene molecule, the approximation $\Delta G^\circ_a = 1/b$ leads to a value of IE(cyclopentanone)$=9.26_9$ eV in excellent agreement with the spectroscopic and equilibrium values.

4.3. Vinyl alcohol

Vinyl alcohol, $CH_2{=}CHOH$, the prototypical enol molecule has been detected in the gas phase as transient during pyrolysis processes, thus allowing the determination of its ionisation energy by electron impact [14] and photoelectron [15] spectroscopy. The values range from 9.0 to 9.3 eV, but a convincing assignement of 9.30±0.05 and 9.17±0.05 eV has been given for the adiabatic IE values of the syn and anti conformers (defined with respect to the arrangement of the CCOH atoms), respectively.

The very short lifetime of neutral vinyl alcohol renders it difficult to be handled in a mass spectrometer, in contrast, it is not the case for the corresponding radical cation which may be prepared from a variety of precursors by electron ionization. We choose to form ionized vinyl alcohol in the external source of the FTICR mass spectrometer by dissociation of ionized cyclobutanol. The following charge transfer reaction is studied in the forward direction:

$$CH_2 = CHOH^{\cdot +} + B \xrightarrow{k_f} CH_2 = CHOH + B^{+} \qquad (1e)$$

The results of our rate constant measurements are summarized in Table 7. The fitting of the data by Eq. (17) (Fig. 5) gives the following parameters values: $a = 0.962 \pm 0.030$, $b = 31.7 \pm 4.0$ eV^{-1}, and $c = 9.268 \pm 0.006$ eV.

Before comparing these data with experiment, some information concerning this system must be recalled. Molecular orbital calculations [16] established that neutral vinyl alcohol, $CH_2{=}CHOH$, is most stable in its syn conformation, the anti conformer being less stable by 4.2 kJ/mol at 298 K. By contrast, ionized vinyl alcohol is more stable in its anti conformation by 7.4 kJ/mol. In keeping with these data, it may be supposed that, under our experimental conditions, only the anti conformer of ionized vinyl alcohol is sampled during reaction (1e) (considering the calculated energy difference of 7.4 kJ/mol between the two conformers and assuming a Boltzmann distribution, the thermalization would lead to 95% of the anti conformer at 298 K). Thus our experimental determination of the ionization energy must be compared with the spectroscopic value concerning the anti conformer.

On the other hand, we found that the rotational barrier separating the syn and anti neutral conformers

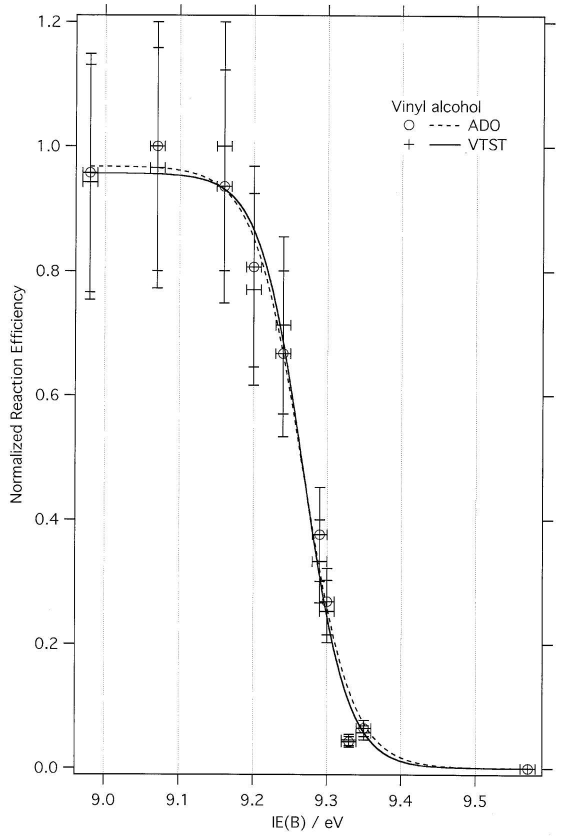

Fig. 3. Normalized reaction efficiencies as a function of IE(B) for the reaction: [cyclopentanone]$^{\cdot +}$+B 154 cyclopentanone+[B]$^{\cdot +}$.

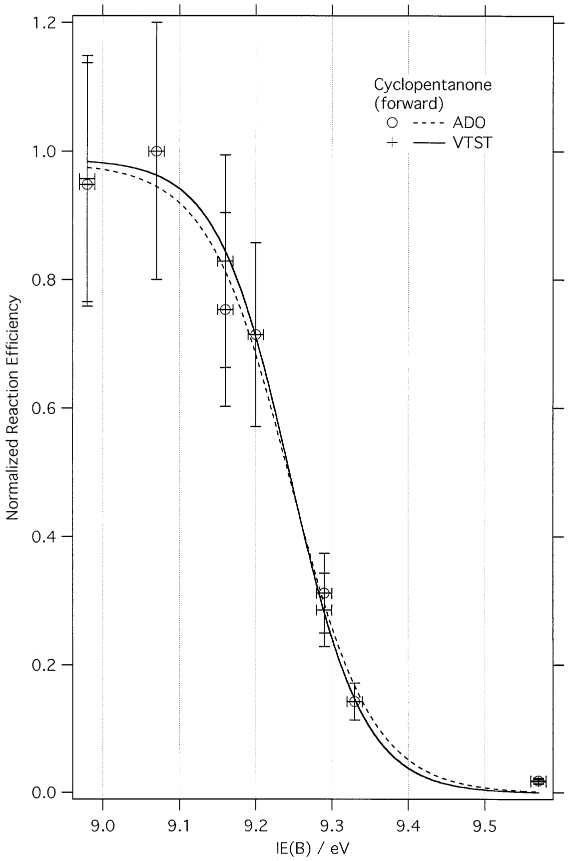

Fig. 4. Normalized reaction efficiencies as a function of IE(B) for the reaction: cyclopentanone+[B]$^{\cdot +}$ 154 [cyclopentanone]$^{\cdot +}$+B.

is small (23 kJ/mol) whereas it attains 90 kJ/mol for the radical cation (ab initio molecular orbital calculations at the MP2/6-31G(*d*) level). One consequence of this large difference in the CO rotational barrier between the molecule and the ion is the existence of a non negligible entropy variation $\Delta_1 S°$. Assuming that $\Delta_1 S° \approx S°(CH_2{=}CHOH) - S°[CH_2{=}CHOH]^{\cdot +}$, and using the Pitzer model [19] to calculate the torsion contribution to $S°(CH_2{=}CHOH)$ and the harmonic oscillator model to calculate $S°[CH_2{=}CHOH]^{\cdot +}$ we obtain $\Delta_1 S° = 6.7\ \mathrm{J\,mol^{-1}\,K^{-1}}$. Therefore, using $IE(M) = c + \Delta_T H° - T\Delta_1 S° + \Delta G°_a$ and assuming that $\Delta_T H° = 0$, one obtains the ionization energy values $IE(CH_2{=}CHOH) = 9.25_8 \pm 0.01_0$ eV with $\Delta G°_a = RT\ln(k_{1c}/k_{2c})$ (0.011 ± 0.005 eV) and $9.27_9 \pm 0.01_0$ eV with $\Delta G°_a = 1/b$ (0.032 ± 0.004 eV). The comparison with the adiabatic ionization energy of the anti conformer of vinyl alcohol (i.e. 9.17±0.05 eV) is correct but reveals a slight overestimate in the thermokinetic results with respect to the spectroscopic value.

A phenomenon, which may account for this overestimate, is the possibility of isomerization of the neutral during the reaction. Accordingly, since the neutral product is more stable in its syn conformation, it is possible that the rotation of the OH group could occur in the charge transfer complex thus favouring the formation of the syn conformer of neutral vinyl alcohol. The consequence of the formation of the syn-$CH_2{=}CHOH$ molecule by electron attachment to the anti-$[CH_2{=}CHOH]^{\cdot +}$ ion is that the term $\Delta_T H°$ is not negligible but equal to −4.2 kJ/mol (−0.044 eV) [16]. Inserting this value in $IE(M) = c + \Delta_T H° - T\Delta_1 S° + \Delta G°_a$ one obtains $IE(CH_2{=}$

Table 7
Parameters relevant to charge transfer reactions: $[CH_2CHOH]^{\cdot+} + B \rightarrow CH_2CHOH + [B]^{\cdot+}$

B	IE(B)[a] (eV)	μ[b] (D)	α[c] ($Å^3$)	k_{exp} ($\times 10^{10}$) ($cm^3\ mol^{-1}\ s^{-1}$)	k_{coll} ($\times 10^{10}$)[d] ($cm^3\ mol^{-1}\ s^{-1}$)	R[e] (%)	$k_{coll(b)}$ ($\times 10^{10}$)[d] ($cm^3\ mol^{-1}\ s^{-1}$)	$k_{coll(f)}/k_{coll(b)}$
Bromobenzene	8.98	1.7	14.7	17.2	19.2 (21.1)	96 (94)	11.5 (12.8)	1.67 (1.65)
Chlorobenzene	9.07	1.7	14.1	18.2	19.7 (21.7)	100 (97)	11.9 (13.3)	1.66 (1.63)
1,4-Difluorobenzene	9.16	0	10.2	11.6	13.3 (13.3)	93 (100)	11.9 (13.3)	1.12 (1.00)
Fluorobenzene	9.20	1.6	10.3	13.4	17.9 (19.9)	81 (77)	12.2 (13.6)	1.47 (1.46)
Benzene	9.24	0	10.2	8.7	14.1 (14.1)	67 (71)	12.7 (14.1)	1.11 (1.00)
1,2-Difluorobenzene	9.29	(2.8)	10.2	8.1	22.9 (27.6)	38 (33)	11.9 (13.3)	1.92 (2.08)
1,2,4-Trifluorobenzene	9.30	(1.6)	10.1	4.19	17.0 (18.9)	27 (25)	11.7 (13.0)	1.45 (1.45)
1,3-Difluorobenzene	9.33	1.6	10.2	0.78	17.4 (19.4)	4 (5)	11.9 (13.3)	1.46 (1.46)
Ethyl iodide	9.35	1.9	10.0	1.07	17.9 (20.5)	6 (6)	11.5 (12.8)	1.56 (1.60)
1,2,3,4-Tetrafluorobenzene	9.57	(2.8)	10.0	0	22.1 (26.6)	0 (0)	11.5 (12.8)	1.92 (2.08)

[a] Ionization energies, from the compilation by Lias et al. [1b,c].

[b] Dipole moment in debye, experimental values from [17] (in parentheses, estimated from comparison with homologous compounds).

[c] Polarizabilities in $Å^3$ calculated using the method of Miller [18].

[d] Collision rate constant calculated using the ADO model [9a] and, in parentheses, trajectory calculations [9b].

[e] Normalized reaction efficiency, $R = (k_{exp}/k_{coll})/(k_{exp}/k_{coll})$ max.

CHOH)$=9.21_4 \pm 0.01_0$ eV with $\Delta G°_a = RT \ln(k_{1c}/k_{2c})$ and $9.23_5 \pm 0.01_0$ eV with $\Delta G°_a = 1/b$. One must emphasize that this value corresponds to the difference in the ground state energies of the anti conformer of ionized vinyl alcohol and the syn conformer of the neutral molecule. It should be compared with the sum of the adiabatic ionization energy of the anti vinyl alcohol and the 0 K enthalpy difference between the two neutral conformers. By using IE(anti-CH_2=CHOH)$=9.17_0$ eV and $\Delta_f H°_0$(anti-CH_2=CHOH)$-\Delta_f H°_0$(syn-CH_2=CHOH) $=0.036$ [16] one obtains a value, 9.20_6 eV, in better agreement with the thermokinetic results. Once again, the choice between the two means to estimate $\Delta G°_a$ cannot be unambiguously decided because the difference between the two estimates (0.02 eV) is comparable to the uncertainty on the measurements. By comparison with the benzene and cyclopentanone molecules, it may be noted that using the effective temperature T_{eff} of 310 K, the approximation $\Delta G°_a = 1/b$ leads to IE(CH_2=CHOH) $=9.23_0$ eV, a value also in correct agreement with the energy difference deduced from spectroscopic values.

5. Conclusion

In summary, the present results demonstrate that the correlation observed between the bimolecular rate constant for the charge transfer reaction

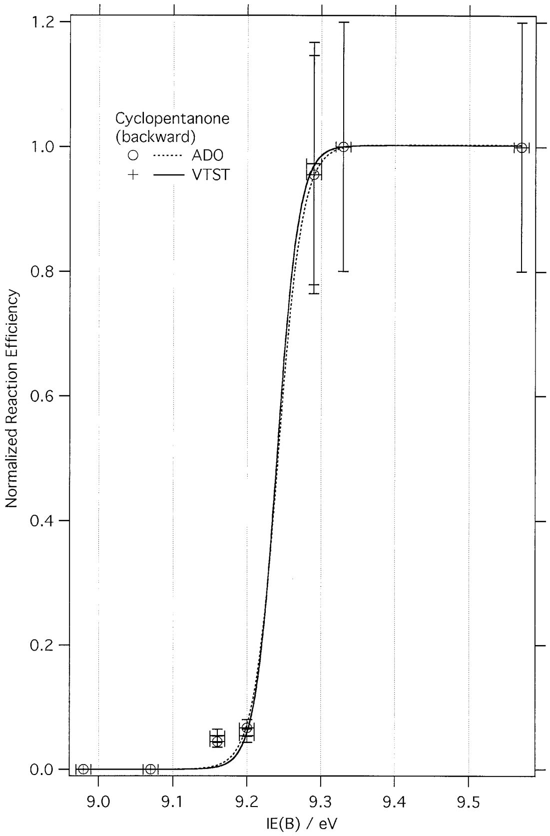

Fig. 5. Normalized reaction efficiencies as a function of IE(B) for the reaction: $[CH_2CHOH]^{\cdot+} + B$ 154 $CH_2CHOH + [B]^{\cdot+}$.

Table 8
Summary of the ionization energy determinations [IE(M) in eV, see text for the detailed explanations].

M	$IE(M)_{eq.}$[a]	$IE(M)_{thermokin.}$[b]	$IE(M)_{spectr.}$[c]
Benzene	$9.24_0 \pm 0.01_3$	$9.24_4 \pm 0.01_2$ $9.26_1 \pm 0.02_5$	9.24378 ± 0.00007
Cyclopentanone	$9.26_5 \pm 0.02_4$	$9.23_7 \pm 0.01_3$ $9.26_9 \pm 0.01_7$	9.263 ± 0.015
Vinyl alcohol	···	$9.21_4 \pm 0.01_0$ $9.23_0 \pm 0.01_0$	$9.206 \pm (.04)$

[a] This work, from equilibrium constant measurement.

[b] This work, from the thermokinetic method. Upper and lower values are obtained using the corrective terms $\Delta G°_a = RT \ln(k_{1c}/k_{2c})$ and $\Delta G°_a = 1/b = 1/RT_{eff}$(with $T_{eff} = 310$K), respectively.

[c] Spectroscopic values.

$M^{\cdot+}+B \rightarrow B^{\cdot+}+M$ and IE(B) may be used to determine IE(M) with a good accuracy. The error of ~±0.01–0.02 eV given in the text for IE(M) is originating from the standard deviation of the fitting parameters. Additional error is expected from the fact that the ionization energies of the reference compounds B are generally given with an accuracy of ±0.01 eV, however, the thermokinetic method which makes use of a set of experimental points would minimize the consequences of this effect. The corrective term $\Delta G°_a$ introduced in the method is theoretically given by $\Delta G°_a = RT \ln(k_{1c}/k_{2c})$, it appears to be conveniently evaluated by the empirical relationship $\Delta G°_a = 1/b = RT_{eff}$ if the effective temperature T_{eff} is equal to the room temperature of the ICR experiments (≈310 K). A summary of the IE(M) values obtained in the present study and of the corresponding spectroscopic data is given in Table 8.

The deviation observed between the "true" spectroscopic values of IE(M) and the estimates based on the thermokinetic approach is less than 0.025 eV for the investigated examples. A similar deviation is associated with the choice of the corrective term $\Delta G°_a$. All in all, it is expected that the thermokinetic method leads to IE(M) values with a precision of ~±0.05 eV (i.e. ±5 kJ/mol). Obviously, examination of other systems is necessary in order to test the generality of these results.

As underlined in Sec. 1, the main advantage of the technique is to allow the measurement of ionization energies for unstable species, one example has been presented with the vinyl alcohol molecule. Applications of the thermokinetic method to the determination of dissociative recombination thresholds and to the detection of isomerization processes during charge transfer reactions are also expected to be realizable.

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