THE CHARGE-EXCHANGE MASS SPECTRUM OF BENZENE

J.M. TEDDER and P.H. VIDAUD

Department of Chemistry, The University, St. Andrews, East Fife KY16 9ST, UK

Received 10 March 1979

The absolute cross section for ionisation and fragmentation of benzene by 29 positive ions of 10 eV kinetic energy and different but known electron recombination energies (eVi) have been determined. A plot of these cross sections against the recombination energies constitutes a charge-exchange mass spectrum of benzene which has certain resemblances to the photoelectron spectrum.

1. Introduction

The study of mass spectra produced by electron transfer was pioneered by Lindholm and co-workers [1]. The present work represents an extension of this technique. The apparatus is a tandem mass spectrometer. Primary ions of known recombination potential eVi are formed by electron impact, selected by a small magnetic sector and then focused into a collision chamber. In the collision chamber the primary ions bombard neutral molecules (benzene in the present experiments), and secondary ions are abstracted at right angles to the primary ion beam, analysed by a large magnetic sector and detected by an electron multiplier. In their earlier study of benzene Jonsson and Lindholm [2] used twelve primary ions to produce a spectrum with eVi varying from 9.2 eV to 24.6 eV. In the present study, twenty-nine ions have been used to cover the smaller range from 8.2 eV to 15.8 eV to reveal a fine structure that could not be seen by Jonsson and Lindholm.

2. Experimental

The details of the apparatus have been described elsewhere [3]. The determined cross sections were virtually independent of the kinetic energy of the primary ions within the range 4.0 eV to 20 eV (see table 1).

These results are in accord with the report of

Table 1

Cross sections, Q_1 and Q_2 , for $C_6H_6^+$ from C_6H_6 by N_2O^+ and NO⁺ respectively as a function of incident ion kinetic energy *E*

<i>E</i> (eV)	Q_1 (10 ⁻¹⁵ cm ²)	Q_2 (10 ⁻¹⁵ cm ²)
4.0	10.6	14.9
6.0	11.7	20.0
8.0	9.8	15.9
10.0	11.5	16.2
15.0	12.6	19.2
20.0	10.2	14 2

Andlauer and Ottinger [4] who found that in chargeexchange reactions of inert gas ions with benzene, the internal energy of the benzene molecules rose only by 0.1 eV when the primary ion's kinetic energy was varied from 10 to 20 eV. The main spectrum shown in fig. 1 was determined using ions with a kinetic energy $10.0 \pm 1.0 \text{ eV}$.

The target gas pressure in the collision chamber was 10^{-4} to 10^{-5} Torr. The flux of primary ions passing into the collision chamber (10^{-8} to 10^{-10} amp cm⁻²) was measured directly by a high voltage ammeter and the absolute cross sections derived using the known cross section for the Ar⁺ + Ar charge-exchange reaction [5]. The absolute cross sections so determined have an error of ± 50% which arises principally from an uncertainty in the collision chamber pressure. However, as the cross sections obtained were indepenVolume 64, number 1

Table 2

Ion	eVi/(eV)	Numeral in fig. 1	Cross section for $C_6H_6^+$ (10^{-15} cm^2)	Total cross section (10 ⁻¹⁵ cm ²)
(CH ₃) ₂ NH ⁺	8.24 ± 0.02	1	1.1	1.1
$C_2H_5NH_2^+$	8.86 ± 0.02	2	1.7	1.7
$CH_2 = CHCH = CH_2^+$	9.06 ± 0.01	3	5.1	5.1
NO⁺	9.264 ± 0.001	4	16.2	16.2
$(CH_3)_2N^+$	9.42 ± 0.002	5	15.0	15.0
NO ⁺ 2	9.75 ± 0.01	б	13.1	13.1
CH ₃ ⁺	9.842 ± 0.002	7	16.3	16.3
SO*	10.0 ± 0.1	8	13.8	13.8
CS_2^+	10.08	9	14.5	14.5
NH_3^+	10.16 ± 0.01	10	13.1	15.0
H ₂ S ⁺	10.47 ± 0.01	11	8-1	10.0
$C_2H_4^+$	10.51 ± 0.03	12	5.7	6.7
CH ₃ OH ⁺	10.85 ± 0.02	13	5.7	5.7
CH ₃ Ci ⁺	11.22 ± 0.01	14	2.9	2.9
$C_2H_2^+$	11.396 ± 0.003	15	8.4	10.0
CS ⁺	11.8 ± 0.2	16	24.3	24.3
0 [*] 2	12.05 ± 0.001	17	24.3	24.3
SO ⁺	12.32 ± 0.01	18	16.8	16.8
H_2O^+	12.62 ± 0.02	19	16.2	20.2
CH ⁺	12.704 ± 0.008	20	18.1	20.0
HCI ⁺	12.74 = 0.01	21	9.2	11.0
N_2O^*	12.894	22	8.5	11.5
OH ⁺	13.18 ± 0.1	23	3.0	3.0
CHN ⁺	13.59 ± 0.01	24	19.7	23.5
CO ⁺ 2	13.769 ± 0.03	25	21.3	28.5
CO ⁺	14.013 ± 0.04	26	15.9	23.0
CN^{+}	14.5 ± 0.2	27	10.6	10.6
N2 ⁺	15.58 ± 0.01	28	6.4	40.0
Ar ⁺	15.757 ± 0.005	29	4.4	28.0

dent of the measured pressure in the range used, the relative cross sections have an accuracy of 10%.

The range of primary ions was limited by the performance of the primary mass spectrometer (e/m from 10 to 70). The primary ion electron recombination energies (eVi) are listed in table 2 and were taken from the ground-state values recommended by Rosenstock et al. [6].

3. Results and discussion

Fig. 1 shows the charge-exchange mass spectrum (CEMS) of benzene compared to the photoelectron spectrum determined by Turner and co-workers [7]. Unfortunately, there are few readily available ions in the correct mass range with accurately known electron recombination potentials eVi greater than 14.0 eV, and the greatest detail has been obtained in the region eVi 8.9 to 13.2 eV where the benzene parent ion $C_6H_6^+$ is the principal secondary species. $C_6H_5^+$ was present throughout the range but only rose to be above 10% of the parent ion signal when eVi approached 13.8 eV which is consistent with the published appearance potential for this ion [6]. The other secondary fragment ions were $C_4H_4^+$, $C_4H_3^+$, $C_4H_2^+$ and $C_3H_4^+$ whose signals only became appreciable in the region between eVi = 14 - 15.5 eV. The presence of weak signals for all the ions below their appearance potential



Fig. 1. (a) Absolute cross sections, Q, for $C_6H_6^+$, (•), and $C_4H_4^+$, (0), as a function of primary ion electron recombination energy, eVi, for primary ions colliding with C_6H_6 with 10 eV of kinetic energy. The numerals identify the primary ions which are listed in table 2. (b) The photoelectron spectrum of C_6H_6 for comparison (from Turner et al. [7]).

is probably attributable to electronically excited primary ions.

The charge-exchange spectrum (fig. 1) for $C_6H_6^{\dagger}$ shows three major peaks with sharp onsets at 9.1, 11.4 and 13 to 13.5 eV, which correspond closely to the onsets of the first three bands in the photoelectron spectrum. The lack of primary ions with electron recombination between 13.18 and 13.59 eV makes the onset of ionisation in the third peak seem less sharp than the first two peaks, but we anticipate that should more primary ions be found with eVi in this region, the onset of this peak will be as sharp as the others. The onset of ionisation in the first peak corresponds to the appearance potential of the $C_6H_6^+$ reported by other techniques [6]. Bregman and co-workers [8] report a cross section of $(15.4 \pm 1.0) \times 10^{-15} \text{ cm}^2$ for the reaction of NO⁺ ions (eVi = 9.2 eV) of 60 eV kinetic energy with benzene. The value for NO⁺ ions of 10 eV kinetic energy obtained in the present work is $(16.2 \pm 8.1) \times 10^{-15} \text{ cm}^2$. A search of the literature failed to reveal any other absolute measurements for the charge-exchange reactions with benzene for the other 28 ions used in the present study.

The first three photoelectron bands at 9.1, 11.4 and 13.8 eV have been ascribed to the $1e_{1g}$, $3e_{2g}$ and $3e_{1u}$ electron ground states of benzene by Asbrink and coworkers [9]. In the charge-exchange mass spectrum little reaction (i.e., negligible secondary ions) is observed until the electron recombination potential of the primary ion approaches the appearance potential of the secondary ion. The most efficient electron transfer will be from the vibrational ground state of the neutral molecule to the vibrational ground state of the primary ion, and this is represented by the sharp onset of ionisation. As the electron recombination potential of the primary ion increases, the reaction will move away from a quasi-resonant state and the cross section will decrease before rising again sharply when the next electron (at 11.4 eV for C_6H_6) can be abstracted.

Although the cross section will be expected to fall off as the difference between the appearance potential of the secondary ion and electron recombination potential of the primary ion increases, this decrease will not exactly follow this energy separation, because the cross section will also depend on the availability of vibrational levels within the Franck—Condon region of the primary ion to primary neutral and the target neutral to target ion [10]. Thus, unlike the photoelectron Volume 64, number 1

spectrum which shows vibrational fine structure belonging to the secondary ion, in exothermic charge-exchange reactions the excess energy appears both in the secondary ion and in the recombined primary bullet. Vibrational structure, even if it could be observed, will, therefore, be extremely difficult to interpret.

The present work shows that charge-exchange spectra (CEMS) can provide an important method of probing the energy levels in polyatomic molecules. Unlike photoionisation, CEMS however requires many experiments to develop a spectrum. The technique also depends upon accurate determination of the electron recombination potential of the primary ions by some other method. Nonetheless, as Lindholm and co-workers originally showed, the technique does have the important advantage of identifying the charged species produced as a result of the exchange reaction. By comparing the charge-transfer cross sections obtained for a given primary ion and target molecules of known CEMS, it may also be possible in certain cases to obtain the primary ion ionisation potentials. If a charge exchange is adiabatic, the onset of charge exchange and photoionisation will be the same for symmetrical molecules since the vertical and adiabatic processes are likely to be similar. However, in asymmetrical molecules the onset of the adiabatic charge-exchange process may precede the onset of vertical photoionisation. At present, work is underway to compare the CEMS of symmetrical and asymmetrical molecules. Preliminary experiments with esters and halogenoalkanes suggest that the onset of ionisation for particular bands

in the CEMS and photoelectron spectra of asymmetrical molecules do differ.

Acknowledgement

The authors wish to thank Dr. J. Jalonen for his criticisms and encouragement and S.R.C. for financial support.

References

- E. Lindholm, in: Ion molecule reactions, Vol. 2, ed. J.L. Franklin (Butterworths, London, 1970) p. 457.
- [2] B.O. Jonsson and E. Lindholm, Arkiv Fysik 39 (1967) 65.
- [3] J. Jalonen, J.M. Tedder and P.H. Vidaud, J. Chem. Soc. Faraday I, to be published.
- [4] B. Andlauer and C. Ottinger, Z. Naturforsch. 27 (1972) 293.
- [5] D. Rapp and W.E. Francis, J. Chem. Phys. 37 (1962) 2631.
- [6] H.M. Rosenstock, K. Dranl, B.W. Steiner and J.T. Herron, J. Phys. Chem. Ref. Data 6 (1977).
- [7] D.W. Turner, C. Baker, A.D. Baker and C.R. Brundle, Molecular photoelectron spectroscopy (Wiley, New York, 1970).
- [8] H. Bregman-Reisler, A. Rosenberg and S. Amiel, J. Chem. Phys. 59 (1973) 5404.
- [9] L. Asbrink, O. Edqvist, E. Lindholm and L.E. Selin, Chem. Phys. Letters 5 (1970) 192.
- [10] M.T. Bowers, W.T. Huntress and J.B. Laudenslager, J. Chem. Phys. 61 (1974) 4600.