ORGANIC MASS SPECTROMETRY, VOL. 21, 193–195 (1986)

Energy Deposition in $[Fe(CO)_5]^{+\cdot}$ Upon Collision With a Metal Surface

Michael J. DeKrey, Hilkka I. Kenttämaa,† Vicki H. Wysocki, and R. G. Cooks‡
Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, USA

Collision of the title ion upon a stainless steel surface at near-normal incidence leads to deposition of internal energy in a well-defined narrow distribution. The energy deposited increases with laboratory collision energy and exceeds 7 eV (average) for 100 eV collisions. The translational-to-vibrational energy transfer efficiency is 15% (assuming an infinitely massive target) at 25 eV collision energy. Comparison is made with the internal energy distributions associated with gas-phase collisional activation using both low and high ion kinetic energies. The narrowness of the distribution of internal energies, the easy access to ions excited to different extents, and the high internal energies accessible, make the ion/surface collision process superior to gas-phase collisional activation for this system.

Various methods of activation are used to characterize gas-phase ions through their dissociation reactions. In spite of their success in many ion structural problems, all of these methods suffer from one or more of the following disadvantages: (i) only a small average amount of energy is deposited,[1–11] (ii) a very broad range of energies is deposited,[2–7,12–17] (iii) only a limited set of ions can be studied (e.g. only ions absorbing certain photons, or only ions having a stable neutral counterpart),[4,8,18–20] (iv) the ion internal energy is not known[5–7,9–17,21] and (v) variation of the ion internal energy in a controlled fashion is not straightforward.[6,7,10,11,17,22] These disadvantages limit the type and number of ions which can be studied, as well as the quality and quantity of information available.

We wish to report our results concerning energy deposition with a promising new ion excitation method, surface-induced dissociation (SID). It is possible to excite organic ions by allowing them to collide with a stainless steel surface at small laboratory energies.[23,24] The extent of fragmentation increases with increasing collision energy, suggesting that there is a dependence of the energy deposition upon the collision energy. We now show that a narrow energy distribution is deposited in these experiments. Furthermore, the amount of energy deposited can be systematically increased up to very high values. Thus, this method allows experiments to be conducted as a function of ion internal energies. The SID method should also be useful in calibrating other activation methods which deposit unknown or ill-defined amounts of energy.

The energy transfer associated with surface collisions can be characterized by ion kinetic energy measurements[25] or by employing a recently developed method[3] for estimating the distribution of internal energies, $P(\varepsilon)$, in a population of ions. The method is based on fragment ion abundances arising from a series of consecutive reactions of similar entropy requirements and known critical energies (ε_0) (Eqn (1)). The relative abundance of the fragment ion $[F_n]^+$, divided by the energy interval $\varepsilon_0(n+1)-\varepsilon_0(n)$, gives a single $P(\varepsilon)$ value which approximately corresponds to the average internal energy in this interval.

$$\underset{\varepsilon_0(1)}{[M]^{+\cdot}\rightarrow}\,\underset{\varepsilon_0(2)}{[F_1]^+\rightarrow}\,\underset{\varepsilon_0(3)}{[F_2]^+\rightarrow}\,[F_3]^+ \qquad (1)$$

The molecular ion of $Fe(CO)_5$ was chosen for this experiment since it loses CO successively by simple cleavage reactions and the critical energies[26] of these reactions are known. Also, this ion has been examined in studies of energy deposition associated with gas-phase collisional activation.[27]

The experiment employed electron impact to generate $[Fe(CO)_5]^{+\cdot}$ (m/z 196), magnetic mass analysis to separate these ions from other species and a quadrupole to analyse the fragmentation products formed upon collision of the selected ions with a metal surface (304 stainless steel). The angles of the incident and emerging beams were selected as 32° and 13° to the normal, respectively. The collision energy was varied over the range 20–130 eV. The apparatus and experimental details are given elsewhere.[23,24] A daughter spectrum of $[Fe(CO)_5]^{+\cdot}$ obtained by SID at a collision energy of 60 eV is shown in Fig. 1. At higher collision energies, the high-enthalpy products $[Fe(CO)]^{+\cdot}$ (m/z 84) and $Fe^{+\cdot}$ (m/z 56) dominate the daughter spectrum, while at lower energies, the higher mass ions including the parent ion itself (m/z 196) make a relatively larger contribution.

The average internal energy deposited in $[Fe(CO)_5]^{+\cdot}$ upon collision can be estimated from the daughter spectrum. For example, Fig. 1 shows that $[Fe(CO)_2]^{+\cdot}$ (m/z 112), $[Fe(CO)]^{+\cdot}$ (m/z 84), and $Fe^{+\cdot}$ (m/z 56) contribute in proportions of 2:8.5:1. From the activation energy data (Table 1), these ions can be ascribed to parents of average internal energy of 4.4 eV, 6.6 eV and 9.2 eV, respectively. (Since there can be no cleavage reaction from $Fe^{+\cdot}$ the

---

† On leave from the Department of Chemistry, University of Helsinki, with a Fellowship from the Academy of Finland.

‡ Author to whom correspondence should be addressed.

0030–493X/86/040193–03$05.00

Received 8 July 1985
Accepted 26 September 1985

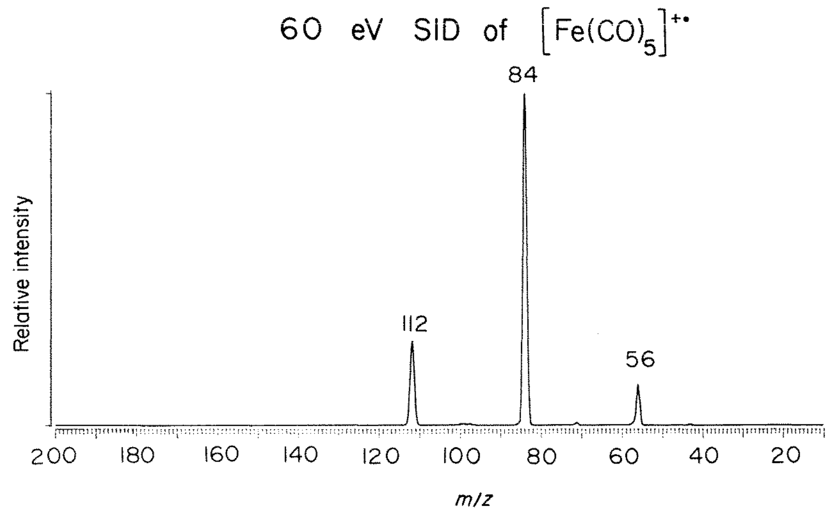

Figure 1. Daughter spectrum due to surface-induced dissociation of $[Fe(CO)_5]^{+\cdot}$ (*m/z* 196) upon 60 eV collision with stainless steel.

Table 1. Thermochemical data used to estimate the energy distributions for $[Fe(CO)_5]^{+\cdot}$

Ion	*m/z*	Critical energy (eV)[a]
$[Fe(CO)_5]^{+\cdot}$	196	0
$[Fe(CO)_4]^{+\cdot}$	168	1.15
$[Fe(CO)_3]^{+\cdot}$	140	2.11
$[Fe(CO)_2]^{+\cdot}$	112	3.33
$[Fe(CO)]^{+\cdot}$	84	5.56
$Fe^{+\cdot}$	56	7.58
$[FeC]^{+\cdot}$	64	15.65[b]

[a] Obtained by subtracting the appearance energy of each fragment from the ionization potential of $Fe(CO)_5$; the appearance energies and ionization potential are selected from Ref. 26.

[b] This ion is observed only in the 7 keV spectrum. Thus, the 7 keV $P(\varepsilon)$ curve must extend to at least 15.65 eV. The presence of this species directs placement of the last point, $Fe^{+\cdot}$, in the $P(\varepsilon)$ curve between $E_0([Fe(CO)]^{+\cdot})$ and $E_0([FeC]^{+\cdot})$.

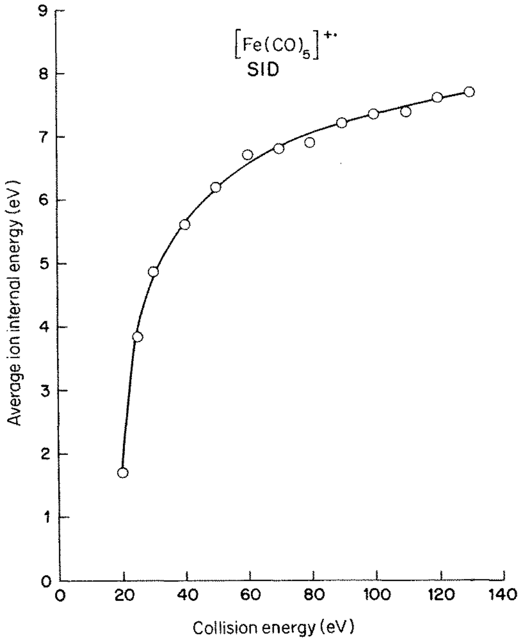

Figure 2. Average internal energy of $[Fe(CO)_5]^{+\cdot}$ after excitation by collision with a surface as a function of the laboratory collision energy. No correction is made for the initial energy of the ion.

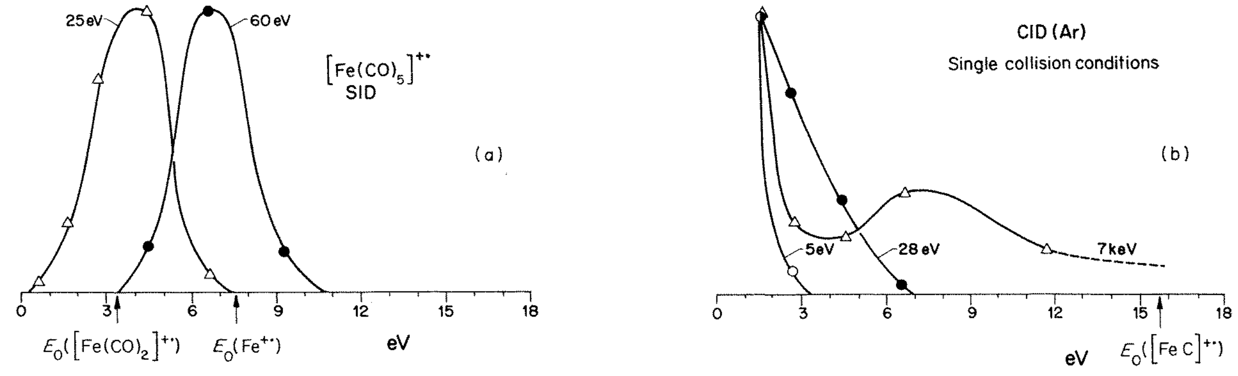

Figure 3. Comparison of internal energy distributions of $[Fe(CO)_5]^{+\cdot}$ after collision (a) at a surface and (b) in the gas phase (single collision upon Ar).

energy interval for $Fe^{+\cdot}$ is an estimate based on the known shape of $P(\varepsilon)$ at lower collision energies.) Combining these values with the ion abundance data and allowing for different symmetry factors yields a weighted average internal energy of 6.6 eV for $[Fe(CO)_5]^{+\cdot}$ ions after a 60 eV collision. The average internal energy increases smoothly and rapidly with laboratory collision energy at low collision energies (Fig. 2), but appears to reach a plateau of *c.* 8 eV at higher collision energies.

It is instructive to consider the energy deposition as a fraction of the available (center-of-mass) kinetic energy. If the surface is considered to be an infinitely massive target, the energy deposited varies from 15% of the theoretical maximum (at 25 eV lab. ion kinetic energy) to less than 7% at high collision energy. A binary collision model,[25] considering the target to be a single Fe atom, yields an energy deposition efficiency which is as large as 73% for 30 eV collisions. This efficiency is high compared to kilovolt energy gas–phase collisional activation experiments.[27,28]

Internal energy distributions estimated by the thermochemical method for fragmenting ions after 25 eV and 60 eV collisions with the surface are shown in Fig. 3(a). The shapes of these distributions are typical of data at other collision energies. The internal energy distributions obtained[27] for gas-phase collision with argon using a triple quadrupole mass spectrometer[29] (eV range) and a reverse-geometry sector instrument[30] (keV range) are given in Fig. 3(b). In comparison with gas-phase collisions, the energy range obtained by SID is remarkably narrow, especially since the ions may have an appreciable distribution of internal energies (up to 1 eV) prior to collision. Furthermore, excellent control of the energy deposition is available, including the possibility of depositing either small or very large amounts of internal energy.

The results presented here demonstrate that surface-induced excitation should be useful in fundamental studies of energy transfer and gas-phase ion chemistry, as well as in analytical applications of mass spectrometry.

Acknowledgements

This work was supported by the National Science Foundation (CHE-8114410A3 and CHE-8408258). HIK acknowledges the support of the Academy of Finland.

REFERENCES

1. C. Lifshitz, *Mass Spectrom. Rev.* **1**, 309 (1982).
2. M. S. Kim and F. W. McLafferty, *J. Am. Chem. Soc.* **100**, 3279 (1978).
3. H. I. Kenttämaa and R. G. Cooks, *Int. J. Mass Spectrom. Ion Proc.* **64**, 79 (1985).
4. H. Ehrhardt, F. Linder and T. Tekaat, *Adv. Mass Spectrom.* **4**, 705 (1968).
5. S. A. McLuckey, C. E. D. Ouwerkerk, A. J. H. Boerboom and P. G. Kistemaker, *Int. J. Mass Spectrom. Ion Proc.* **59**, 85 (1984).
6. D. M. Fedor, R. B. Cody, D. J. Burinsky, B. S. Freiser and R. G. Cooks, *Int. J. Mass Spectrom. Ion Phys.* **39**, 55 (1981).
7. R. B. Cody and B. S. Freiser, *Anal. Chem.* **51**, 547 (1979).
8. F. M. Harris and J. H. Beynon, in *Gas Phase Ion Chemistry*, ed. by M. T. Bowers, Vol. 3, Academic Press, New York (1984).
9. W. Brand and K. Levsen, *Int. J. Mass Spectrom. Ion Phys.* **35**, 1 (1980).
10. S. A. McLuckey, *Org. Mass Spectrom.* **19**(11), 545 (1984).
11. D. M. Fedor, R. B. Cody, D. J. Burinsky, B. S. Freiser and R. G. Cooks, *Int. J. Mass Spectrom. Ion Phys.* **39**, 55 (1981).
12. D. D. Fetterolf and R. A. Yost, *Int. J. Mass Spectrom. Ion Phys.* **44**, 37 (1982).
13. J. A. Larameé, P. H. Hemberger and R. G. Cooks, *Int. J. Mass Spectrom. Ion Phys.* **33**, 231 (1980).
14. K. Levsen and H. Schwarz, *Angew. Chem. Int. Ed. Engl.* **15**(9), 509 (1976).
15. P. J. Todd and F. W. McLafferty, *Int. J. Mass Spectrom. Ion Phys.* **38**, 371 (1981).
16. S. Verma, J. D. Ciupek and R. G. Cooks, *Int. J. Mass Spectrom. Ion Proc.* **62**, 219 (1984).
17. K. R. Jennings, *Gazz. Chim. Ital.* **114**, 313 (1984).
18. J. J. Zwinselman and A. G. Harrison, *Int. J. Mass Spectrom. Ion Proc.* **62**, 187 (1984).
19. A. G. Brenton, R. P. Morgan and J. H. Beynon, *Ann. Rev. Phys. Chem.* **30**, 51 (1979).
20. T. Baer, in *Gas Phase Ion Chemistry*, ed. by M. T. Bowers, Vol. 1, Academic Press, New York (1979).
21. K. Levsen, *Fundamental Aspects of Organic Mass Spectrometry*, Verlag Chemie, Weinheim—New York (1978).
22. G. Mauclaire, R. Derai, S. Fenistein and R. Marx, *J. Chem. Phys.* **70**, 4017 (1979).
23. Md. A. Mabud, M. J. DeKrey and R. G. Cooks, *Int. J. Mass Spectrom. Ion Proc.*, **67**, 285 (1985).
24. M. J. DeKrey, Md. A. Mabud, R. G. Cooks and J. E. P. Syka, *Int. J. Mass Spectrom. Ion Proc.*, **67**, 295 (1985).
25. W. Heiland and E. Taglauer, in *Inelastic Ion–Surface Collisions*, ed. by N. H. Tolk and J. C. Tulley, p. 27, Academic Press, New York (1977).
26. H. M. Rosenstock, K. Draxl, B. W. Steiner and J. T. Herron, *J. Phys. Chem. Ref. Data* **6**, Suppl. 1 (1977).
27. V. H. Wysocki, H. I. Kenttämaa and R. G. Cooks, submitted for publication.
28. F. W. McLafferty (Ed.), *Tandem Mass Spectrometry*, John Wiley and Sons, New York (1983).
29. J. R. B. Slayback and M. S. Story, *Ind. Res. Dev.* February, 129 (1981).
30. J. H. Beynon, R. G. Cooks, J. W. Amy, W. E. Baitinger and T. Y. Ridley, *Anal. Chem.* **45**, 1023A (1973).