NOTIZEN

Heat of Formation of the HCO Radical

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Dedicated to Prof. Dr. W. Groth on his seventieth birthday

From the threshold of OH^+ formation in the photoionisation of formic acid the heat of formation of the HCO radical is determined as 10.2 Kcal/mole, in agreement with the earlier value derived from photoionisation of formaldehyde.

A recent study of the photoionisation of formaldehyde[1] has revealed the occurence of the process

$$CH_2O + h\nu \rightarrow H^+ + HCO \qquad (1)$$

at wavelengths less than (71.2 ± 0.3) nm corresponding to a threshold energy of (17.41 ± 0.07) eV. From this value the heat of formation of the HCO radical was determined as (9.9 ± 1.6) kcal/mole with the assumption that any excess kinetic or internal energy of the products of reaction (1) is negligible at the threshold. The formyl radical is an important intermediate in hydrocarbon oxidation processes and its heat of formation as well as the H – CO bond dissociation energy are of considerable interest. The interest is heightened by a longstanding dispute regarding the choice between two values for ΔH_f (HCO) offered by various experimental evidence. The history of the dispute will not be reviewed here[2], but it is clear that the question should be settled. Hence, it was desirable to supplement the photoionisation data from formaldehyde with similar observations on other substances. Below we report results for formic acid and acetaldehyde. These compounds were selected for the purpose of the present study, because they had been found suitable in the determination of the heat of formation of the formyl ion, also by photoionisation mass spectrometry[3]. The vapor pressures in the ion source region were kept below 10^{-3} Torr to avoid dimerization, specifically in the case of formic acid. All other pertinent details of the instrumentation and techniques were the same as described previously[1, 4].

Table 1 summarizes the appearence potentials for the major ions observed in the photoionisation of formic acid and acetaldehyde. The thresholds were determined by plotting the ratio of ion current to light intensity as a function of wavelength and extrapolating to zero. The values assembled in Table 1 are obtained after correction for the limited spectral resolution (0.35 nm). The parent ion thresholds are in good agreement with the values of Watanabe et al.[7] from measurements with a photoionisation chamber, and the M 44 and M 43 thresholds for acetaldehyde are also in good agreement with the values given by Hurzeler et al.[8] obtained by photoionisation with mass analysis. The implications of the M 29 thresholds were discussed previously[3]. A M 45 photoionisation threshold for formic acid has not yet been reported. The present determination provides the heat of formation of the CO_2H^+ ion, $\Delta H_f\,(CO_2H^+) = 140.9 \pm 0.7$ kcal/mole, where the uncertainty refers to that of the threshold determination. The most recent electron impact value[9], from acetic acid, is 145 kcal/mole. The structure of the CO_2H^+ ion is unknown. If it were identical with that of the ion resulting from the protonation of CO_2, its heat of formation would also determine the CO_2 proton affinity PA (CO_2). Using this assumption we calculate from the well-known heats of formation[10] for H^+ and CO_2 the value PA $(CO_2) = 5.73 \pm 0.03$ eV which coincides with the upper limit value set by Roche et al.[11] from proton transfer reaction chemistry.

The threshold behavior of the ions M15 and M17 generated in the photoionisation of acetaldehyde

Table 1. Threshold energies of the major ions in the photoionisation of formic acid and acetaldehyde.

Compound	*m/e*	Treshold Value (nm)	(eV)	Remarks
HCOOH	46	111.0 ± 0.3	11.16 ± 0.03	Ionisation potential
	45	100.9 ± 0.3	12.29 ± 0.03	$\Delta H_f\,(CO_2H^+) = 6.11 \pm 0.03$ eV[a]
	29	96.9 ± 0.3	12.79 ± 0.03	see discussion Ref. [3]
	17	69.0 ± 0.2	17.97 ± 0.06	ΔH_f (HCO) $= 0.44 \pm 0.06$ eV[a]
CH_3CHO	44	121.5 ± 0.3	10.20 ± 0.02	Ionisation potential
	43	114.6 ± 0.3	10.82 ± 0.03	Ref. [10]: 11.1 ± 0.02 eV
	29	105.1 ± 0.3	11.79 ± 0.03	see discussion Ref. [3]
	15	87.9 ± 0.3	14.11 ± 0.05	AP (Process 2) $= 14.17$ eV

[a] using ΔH_f (HCOOH) $= -3.919$ eV, Ref. [5, 6].

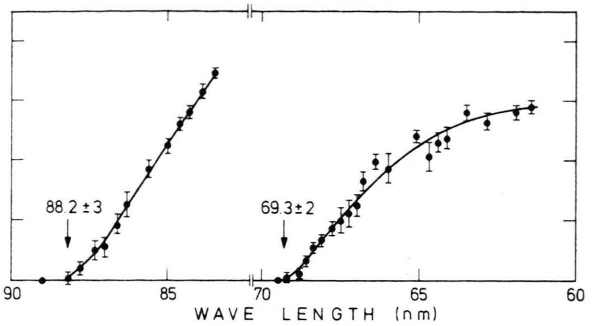

Fig. 1. Relative ion yields in arbitrary units as a function of wavelength for the ions $m/e=15$ in the photoionisation of acetaldehyde, and $m/e=17$ in the photoionisation of formic acid. Employed light source: argon spark discharge.

and formic acid, respectively, are reproduced in Fig. 1 to show that in both cases the relative ion yield rises steeply. Hence the threshold energies are well defined with a minimum uncertainty. In the wavelength region 64 – 67 nm the density and intensities of the lines produced by the argon spark source are less than in other regions of the spectrum, so that a larger scatter results. However, in the regions of the thresholds the density and intensity of lines is sufficient to provide data points at wavelength intervals of no more than 0.3 nm, despite the limited resolution.

The appearence potential observed for the M15 ion in the photoionisation of acetaldehyde coincides almost exactly with that calculated for the process.

$$CH_3CHO + h\nu \rightarrow CH_3^+ + CO + H \qquad (2)$$

from known thermochemical data [6, 10]. The sharpness of the onset indicates that the stable products CH_3 and HCO cannot be reached by the optical process in a measurable yield. The CH_3^+ ion in reaction (2) probably derives by fragmentation of the CH_3CO^+ ion. On the other hand, the threshold energy for the M17 ion produced in the photoionisation of formic acid lies well below that calculated for the products OH^+, CO, and H so that at least at the threshold the occurence of the M17 ion can be identified with the process

$$HCOOH + h\nu \rightarrow OH^+ + HCO\,. \qquad (3)$$

Subtracting from the measured threshold energy, (17.97 ± 0.06) eV, the ionisation potential [10] of OH (13.18 eV) provides immediately the dissociation energy for the M17 ion produced in the photo- ± 0.06) eV or (110.4 ± 1.3) kcal/mole, where as above the uncertainty is that of the threshold determination. With the heats of formation [5, 6, 10] for OH^+ and HCOOH one obtains from the threshold energy for process (3) the heat of formation of the formyl radical, ΔH_f (HCO) = (10.2 ± 1.3) kcal/mole. This value corresponds to the higher of the two values discussed in the literature [2]. It is in excellent agreement with the value 9.9 kcal/mole derived from the photoionisation of formaldehyde and substantiates our earlier conclusions [1]. Accordingly, we suggest from the average of the two determinations, ΔH_f (HCO) = (10.1 ± 1.3) kcal/mole as the currently most acceptable value for the heat of formation (at 298 °K) of the formly radical.

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[1] P. Warneck, Z. Naturforsch. **26 a,** 2047 [1971].

[2] see J. A. Kerr, Chem. Rev. **66,** 465 [1966].

[3] C. S. Matthews and P. Warneck, J. Chem. Phys. **51,** 854 [1969].

[4] W. P. Poschenrieder and P. Warneck, J. Appl. Phys. **37,** 2812 [1966]; Analyt. Chem. **40,** 385 [1968].

[5] G. C. Sinke, J. Phys. Chem. **63,** 2063 [1959].

[6] R. R. Bernecker and F. A. Long, J. Phys. Chem. **65,** 1565 [1961].

[7] K. Watanabe, T. Nakayama, and J. Mottl, J. Quant. Spectry. Radiative Transfer **2,** 369 [1962].

[8] H. Hurzeler, M. G. Inghram, and J. D. Morrison, J. Chem. Phys. **28,** 76 [1958].

[9] M. A. Haney and J. L. Franklin, Trans. Faraday Soc. **65,** 1794 [1969].

[10] D. R. Stull and H. Prophet, Janaf, Thermodynamic Tables, National Standard Reference Date Series, National Bureau of Standard, 37, U.S. Dept. of Commerce (1971).

[11] A. E. Roche, M. M. Sutton, D. K. Bohme, and H. I. Schiff. J. Chem. Phys. **55,** 5480 [1971].